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Design and Development of a Continuous-Flow Countercurrent Metal Extraction System to Remove Heavy Metals from Contaminated Soils

by *C. Nelson Neale, R. Mark Bricka, WES*
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Design and Development of a Continuous-Flow Countercurrent Metal Extraction System to Remove Heavy Metals from Contaminated Soils

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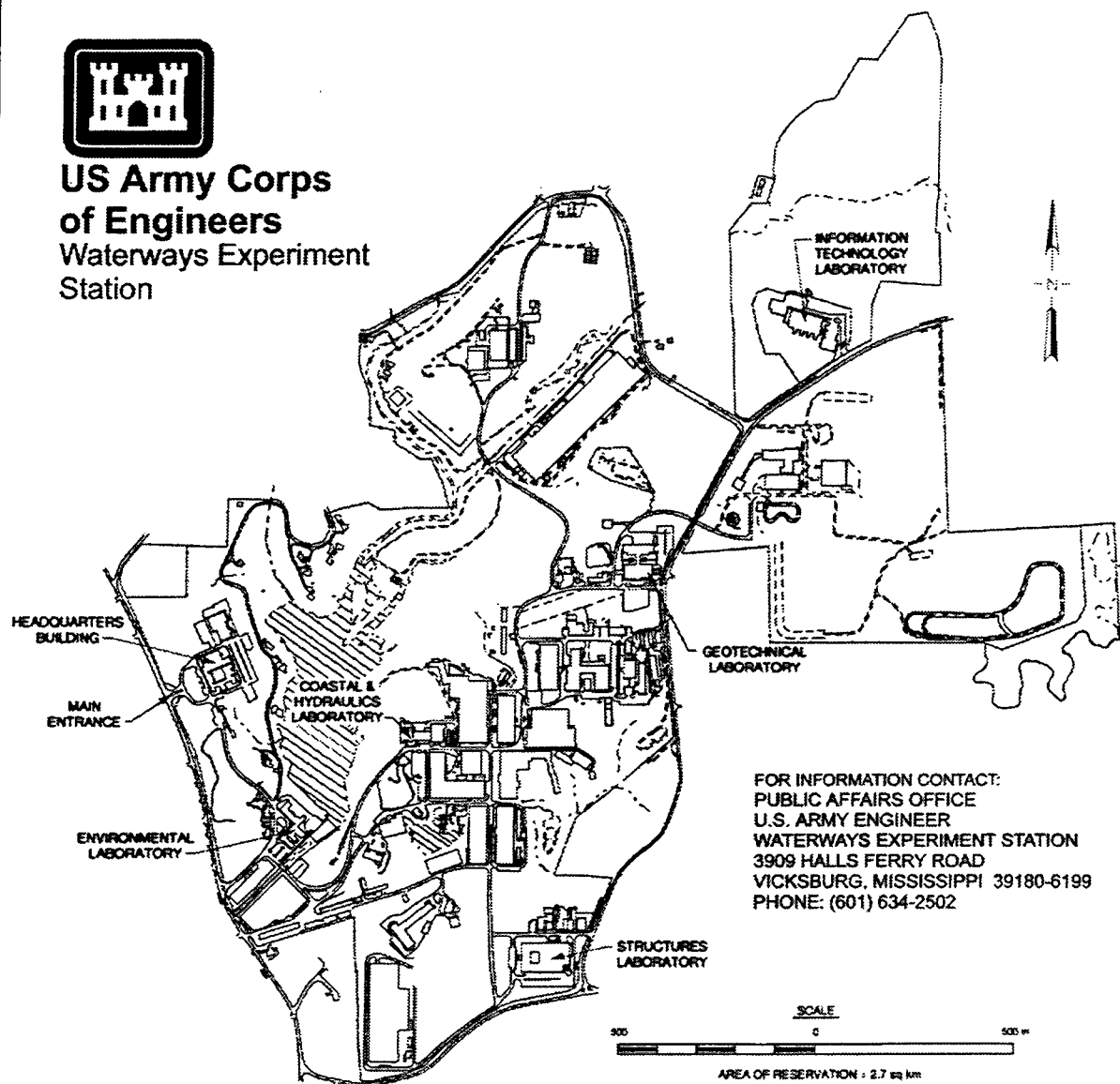
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Preface

The work reported herein was conducted by the U.S. Army Engineer Waterways Experiment Station (WES) as part of the Installation Restoration Research Program (IRRP) under Program AF-25 Work Package 306 on Heavy Metals Treatment Technologies. Dr. Clem Myer was the IRRP Coordinator at the Directorate of Research and Development, Headquarters, U.S. Army Corps of Engineers (HQUSACE). Dr. Bob York of the U.S. Army Environmental Center and Mr. Jim Ballif of the Environmental Restoration Division, Directorate of Military Programs, HQUSACE, served as the IRRP Overview Committee. Technical Monitor for this effort was Mr. Jim Jenkins, Assistant Chief of Staff for Installation Management/ Office of the Director of Environmental Programs. Dr. John Cullinane, WES, was the IRRP Program Manager.

The work was performed during the period December 1994 - June 1996 by Mr. C. Nelson Neale and Mr. R. Mark Bricka, Environmental Restoration Branch (ERB), Environmental Engineering Division (EED), Environmental Laboratory (EL), WES, and Dr. Allen C. Chao, North Carolina State University, Civil Engineering Department, under contract to WES. Special assistance for this work was provided by Ms. Carla Guimbellot, Dr. Drew Wilke, and Ms. Linda Bowling, WES.

The work was conducted at WES under the direct supervision of Mr. Daniel E. Averett, Chief, ERB, and under the general supervision of Mr. Norman R. Francingues, Chief, EED, and Dr. John Harrison, Director, EL.

At the time of publication of this report, Director of WES was Dr. Robert W. Whalin.

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Conversion Factors, Non-SI to SI (Metric) Units of Measurement

Non-SI units of measurement used in this report can be converted to SI (metric) units as follows:

Multiply	By	To Obtain
degrees (angle)	0.01745329	radians
gallons (U.S. liquid)	3.785412	liters
inches	2.54	centimeters
tons (2,000 pounds, mass)	907.1847	kilograms

1 Introduction

Hundreds of sites in the United States have been heavily polluted with organic and trace metal contaminants resulting from various activities including electroplating, metal working, battery recycling, solvent manufacturing, etc. As a result of such widespread contamination, Congress has passed legislation designed to reduce the production of pollutants, control the discharge of these species, and remediate sites where the contamination causes serious environmental problems.

Hazardous Waste Regulations

Three of the more prominent Acts promulgated by Congress include the Resource Conservation and Recovery Act (RCRA) (40 CFR 260, Subtitle C), the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) (Lee 1993) (40 CFR 300), and the Federal Facilities Act (FFA) (40 CFR Subpart K) (Code of Federal Regulations 1992). Together, these laws define hazardous substances and their constituents as well as outline regulations governing the generation, transport, storage, disposal, and cleanup of these wastes.

RCRA

RCRA (promulgated in 1980) lists specific hazardous materials that must be monitored and possibly treated before disposal. These materials are separated into four categories: listed wastes, characteristic wastes, listed mixture wastes, and characteristic mixture wastes.

Listed wastes are known hazardous substances that are further divided into four categories according to the following characteristics: K-Specific, F-Non-specific, P-Acute, and U-Non-acute. K and F Listed wastes indicate whether a hazardous substance was generated from a nonspecific source or was generated through a specific process such as rinsewater from a metal-plating facility. P and U Listed wastes, refer to the toxicity level of the waste. A complete listing of these substances can be found in 40 CFR 261.32.

Characteristic wastes are those substances that exhibit the properties of toxicity, corrosivity, ignitability, or reactivity. A listed mixture waste is a listed waste that

has been combined with another substance. Like listed mixture wastes, characteristic mixture wastes are characteristic wastes that have been mixed with another substance (40 CFR 260.21).

A comprehensive United States Environmental Protection Agency (USEPA) standard toxicity characteristics leaching procedure (TCLP) is performed on some types of waste or soil samples collected from process streams or soils that are suspected of posing ecological risk. If any of the hazardous constituents of the waste are present in the TCLP extract in concentrations that exceed the minimum concentration level established by the USEPA, the waste must be disposed of in an RCRA-approved hazardous waste landfill. State and local authorities can further stipulate more stringent cleanup criteria. In many instances, a contaminated soil can pass the Federally mandated TCLP, but fail to meet the minimum concentration standards mandated by State agencies.

The Hazardous and Solid Waste Amendments substantially modified RCRA regulations in 1984. According to these regulations, the contaminated material that is removed from a site cannot be disposed in a landfill unless it has been treated to meet certain cleanup standards. These regulations may pose a problem for site remediation activities that use the "dig and haul" approach since, in many instances, the contaminated material is currently being excavated and sent to an RCRA-approved landfill without any treatment.

CERCLA

CERCLA, also referred to as Superfund, addresses sites that are already contaminated with hazardous materials. CERCLA outlines a ranking scheme to determine the health and environmental risks associated with hazardous waste. If the risks are significant, the site will be prioritized on the National Priority List (NPL). NPL sites are considered to be the most contaminated sites thus receiving priority attention and cleanup actions. The financial responsibility of site remediation is assumed by potentially responsible parties, which refer to those persons or industries that are responsible for the pollution.

FFA

In an effort to address widespread contamination at U.S. Department of Energy (DOE) and Department of Defense (DOD) sites, Congress added a special section to CERCLA known as the Federal Facilities Act. This Act established a listing of the most heavily contaminated Federal sites based on many of the same factors used in NPL rankings. To fund cleanup of these sites, DOE and DOD established the Defense Environmental Restoration Program funded by Congress through the Defense Environmental Restoration Account (Lee 1993). As required by RCRA, CERCLA, and FFA, industrial and Federal sites contaminated with hazardous materials must develop strategies for site remediation.

Overview of Current Soil Treatment Technologies

The U.S. Army Engineer Waterways Experiment Station (WES) is responsible for developing treatment technologies under the Army's installation restoration program to assist in remediation of Federal facilities contaminated with hazardous substances (Bricka, Williford, and Jones 1993). Although the cleanup of numerous hazardous materials is being investigated, the Army has recognized that heavy metals contamination deserves a greater allocation of military resources because of its predominance at Army sites and the lack of technology to address such contaminants.

The majority of historical metal contamination at military sites is found in firing range soils, ammunitions manufacturing facilities, weapons manufacturing facilities, and electroplating and metal workshop areas, as well as incineration rinse-water lagoons and weapon and debris disposal areas. In fact, heavy metals currently constitute five of the six most cited hazardous materials at Army sites (Bricka, Williford, and Jones 1993). Metals frequently found at military sites are lead (Pb), cadmium (Cd), and chromium (Cr). All of these metal elements are toxic to human health causing a variety of ailments including brain/ neurological damage, liver and kidney damage, and cancer (*Technological Profile for Cadmium Draft* 1987; *Technological Profile for Chromium Draft* 1987). Their contaminant pathways include ingestion of contaminated water, soil ingestion usually resulting from poor hygiene, soil absorption through the skin, and dust/vapor inhalation.

To address these threats to human health, a limited number of technologies have been developed for treating and/or disposing of soils polluted with heavy metals. The advantages and disadvantages of some of the more pertinent technologies are discussed in the following sections.

"Dig and haul"/landfilling

Perhaps the most widely used remediation technique involves excavating soils contaminated with hazardous materials and disposing of the contaminated soils off-site, usually in RCRA-approved landfills. Currently, the cost of disposing contaminated soils in a hazardous waste landfill ranges approximately between \$2,000 and \$2,500 per cubic yard (Bricka, Williford, and Jones 1993). Stringent regulations governing the operation of hazardous waste landfills and dwindling landfill space are constantly increasing the cost of burying contaminated soil, thereby making this alternative less desirable. Additionally, monitoring of soil and groundwater at the landfill will still be necessary, making the cost of implementing such a strategy more prohibitive (Royer, Selvakumar, and Gaire 1991). More alarming than the costliness of the technology is the fact that the landfilling approach remains flawed because contaminants are merely transferred from one site to another. With dig and haul techniques, contaminants in the soil do not undergo any treatment to be either immobilized or kept from leaching from the soil.

Soil capping

Capping uses a cover placed over contaminated soil sites to reduce off-site contaminant migration. Either a single-layer or multilayer system of highly impermeable synthetic membranes or clay layers can be used for capping the contaminated soil. This cap prevents infiltration of precipitation into the contaminated site, thus preventing the water from percolating through the waste providing a pathway to potentially contaminate groundwater supplies. Full site containment and economic feasibility are two major advantages of the soil capping technique (Royer, Selvakumar, and Gaire 1991). However, as with landfilling, the contaminants in the capped waste are neither treated nor removed.

Solidification/stabilization

Solidification/Stabilization (S/S) is a technology with full-scale application that does involve treatment of the contaminated soil. Contaminated soils are mixed with binding agents such as cement, fly ash, pozzolanic concrete, lime, or kiln dust. In many S/S processes, monolithic blocks are produced with enhanced chemical and physical characteristics. This treatment is designed to immobilize the hazardous contaminants.

The binding agents perform two functions. First, the chemicals within the binding agents immobilize soluble metals through partial chemical bonding. The new soil matrix reduces the potential for leaching of substances into groundwater supplies. Second, the binding agents alter the physical properties of the soil by increasing strength and decreasing compressibility and permeability. Since the pH of the binding agents is usually high, remobilization of metals from hydroxide and carbonate salt states is very unlikely (LaGrega, Buckingham, and Evans 1994).

A variety of tests can be performed on the solidified material to measure both its chemical and physical nature after stabilization. Some of these tests include the TCLP and the Sequential Leach Test, which measure the leachability of the contaminants, as well as the Cone Index and the Unconfined Compressive Strength Tests, which gauge the material's strength and ability to handle large pressure loads (LaGrega, Buckingham, and Evans 1994).

Studies at several contaminated sites monitored by the USEPA have shown that S/S effectively immobilized contaminants in soils (Royer, Selvakumar, and Gaire 1991). Although this technique reduces the mobility of contaminants, its application has two major concerns. First, metals are not removed from the soil, thereby providing the potential for contaminant migration in the future. Thus, the generator of the waste is left with long-term liability. Second, binding agents may break down after several years leading to contaminant remobilization. If this occurs, the soil will either have to be resolidified or remediated with alternative techniques.

Vitrification

Vitrification (or glassmaking) stabilizes trace metals in soils through the conversion of contaminated soil into basalt glasslike, noncrystalline materials using high temperature meltdown followed by rapid cooling (Royer, Selvakumar, and Gaire 1991). This high temperature thermal conversion is achieved by placing electrodes into the soil while graphite and glass frit are placed on top of the soil to serve as starter materials. A current is applied to the graphite and embedded electrodes creating a high temperature zone that causes meltdown of the soil at a rate of 4 to 6 tons¹ per hour (LaGrega, Buckingham, and Evans 1994). Once the soil cools, contaminants are permanently retained in glass forms. Volume reduction is a major advantage of the vitrification technique. When heat is applied, the liquid in the soil is evaporated, thus reducing the original volume of contaminated soil. In addition, the vitrified soil is highly resistant to contaminant leaching; however, the process does require a great amount of energy to achieve desired temperatures for meltdown, and the soil matrix is destroyed instead of being salvaged.

Ion exchange

Ion exchange is a treatment process in which metals in solution are substituted with exchangeable ions from either synthetic resins or clays. These resins and clays usually have high exchange capacities because their ion functional groups easily bind with cationic ions in the contaminated solution (Royer, Selvakumar, and Gaire 1991). The ion exchange process can be easily implemented. First, the solution and resin (or clay) are mixed, leading to an exchange between less harmful ions in the medium with metal ions contained in solution. This can be implemented using a column or batch process. In a batch process, the solution and solid are separated through sedimentation or centrifugation. This process is widely recognized in water softening applications where sodium (Na^+) ions in the resin replace calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions in the water that cause hardness. Factors that affect this process include pH, cation competition, and the presence of complexing agents.

To initiate ion exchange in the field for soil remediation, synthetic or clay mediums are introduced into the soil through creation of a slurry containing both contaminated soil and medium (Bricka, Williford, and Jones 1994). After a suitable contact time, the resins that contain high concentrations of contaminants are removed. Advantages of this process include commercial availability of processing units, low energy costs, and the potential regeneration of synthetic resins. The major disadvantage of ion exchange is associated regeneration or disposal costs if regeneration is not possible or cost prohibitive (Royer, Selvakumar, and Gaire 1991).

¹A table of factors for converting non-SI units of measurement to SI units is presented on page ix.

Electrokinetics

Electrokinetic remediation of soil is a rapidly emerging and potentially cost-effective technology that centers on the use of an electrical potential to move charged contaminants toward electrodes of opposite charge. Graphite or other conducting metal electrodes are placed in situ on either side of the contaminated soil mass. Through current application, an acidic front is propagated at the anode and assists in the release of soluble metals into the pore fluid. Simultaneously, a basic front is created at the cathode that moves toward the anode. Amendments are added to the cathode to keep soil pH below 7 in this remediation system to reduce soil pore clogging caused by metal precipitation (Hamed, Acar, and Gale 1991). The electrode fluid having elevated concentrations of metals is extracted and treated to remove the contaminants (Hamed, Acar, and Gale 1991).

Soil washing

Unlike processes that reduce the leachability of contaminants, soil washing focuses on chemical leaching to remove metals from contaminated soil. This process of leaching contaminants from the soil particles into solution is generally achieved through two distinct processes: (a) physical separation of the contaminated soil particles, and (b) chemical extraction of the metal contaminants. Physical separation reduces the volume of soil that has to be chemically treated. Chemical extraction breaks the metal-soil bonds, forcing contaminants into solution. A detailed description of the two mechanisms is outlined below.

Physical separation. Physical separation processes attempt to separate soil fractions using differences in particle size, density, surface area, and magnetism (Bricka, Williford, and Jones 1994). In general, particles with small diameters have the ability to retain or adsorb a greater quantity of metals per unit weight of soil particles because they have relatively large surface areas that are capable of metal bonding.

The physical separation process begins with a characterization of the soil to determine the location and extent of contamination. Samples of the contaminated soil are thoroughly homogenized to ensure uniform distribution of particles and contaminants. Once homogenized, the soil is separated into distinct size fractions.

The separation process is accomplished through several stages beginning with an initial screening to remove oversized particles. The remaining fraction is further processed to isolate finer fractions using mechanical shaking sieves or trommel screens. The particles that pass through the sieve or screen are further classified, while the larger particles are removed for disposal or onsite backfilling, depending on their contamination level. Separation of the fine particles can be accomplished using equipment that includes spiral concentrators or hydrocyclones.

If separation is effective in concentrating the metal contaminants in a smaller soil volume, the less contaminated soil is backfilled; the concentrated fraction can then be treated using chemical extraction techniques.

Chemical extraction. Chemical extraction, the focus of this study, is a process in which the contaminated soil is mixed with an extracting agent or solvent that is capable of desorbing the contaminant from the soil particle surface into solution. Usually, only the most heavily contaminated soil fraction is treated by use of the chemical extraction process, due to the cost associated with this treatment.

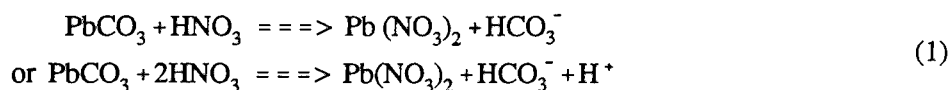
Both organic and metal contaminants in soil can be removed by use of the extraction processes by tailoring the process using organic solvents, acids, chelating agents, or supercritical fluids. In the case of organic contaminant removal, solvents such as ethanol and acetone are used to desorb the contaminants from the organic matter (Piersynski, Sims, and Vance 1994; Markiewicz and McGovern 1992). Acids, bases, and chelating agents are the major extracting agents used to leach metal contaminants from soil. These chemicals react to solubilize metals that are bound to various soil fractions. Acids solubilize metals through ion exchange, while chelating agents solubilize metals through complexation.

For effective metal removal, the contact period between soil particles and the extracting agent should be sufficient for the chemical reactions to approach equilibrium. Once contaminant transfer reaches equilibrium, mixing and reaction are ceased, and the solids and liquid are separated using treatments that include filtration, centrifugation, or reverse osmosis. The metal-enriched solution can be further concentrated or recycled depending on the metals content.

Numerous studies have been devoted to the subject of chemical equilibrium between metal contaminants in soils and extracting agents. For example, when extracting metals from contaminated riverbed sediment using magnesium chloride (MgCl_2) and hydrochloric acid (HCl), Trefry and Metz (1984) found that the reaction time to reach equilibrium was less than 12 hr for Cd, copper (Cu), and zinc (Zn), while more time was needed to reach equilibrium for Pb. In contrast, Peters and Shem (1991) determined that metal removal was dependent on the type of extracting agent used. Using a spiked soil, Peters determined the time to reach equilibrium for ethylenediaminetetraacetic acid (EDTA) and Pb was 1 hr, while the reaction between nitrilotriacetic acid (NTA) and Pb reached equilibrium in 3 hr. These findings indicate that soil-extracting agent equilibrium may depend on several factors, including the type of soil, type and concentration of extracting agent, and soil contaminant.

Since this research focuses on the removal of metals from contaminated soil, the function of acids and chelating agents as metal extracting agents is further explored.

Acids. Acids dissociate in aqueous solution to become proton donors. When mixed with a metal-contaminated soil, these protons replace or exchange with the metal ions that are bound to the soil. Equation 1 is a typical example of an acid extraction involving Pb^{2+} sorbed to the carbonate fraction of soil mixed with nitric acid (HNO_3):



Typical acids used in metal extraction include HNO_3 , HCl , and hydrofluoric acid (HF). Although acids effectively increase the solubility of metals, strong acids tend to destroy the basic structure of the soil (Bricka, Williford, and Jones 1993). This destruction of the soil matrix can leave the soil unsuitable for revegetation and reuses. Given the potential destructive nature of acids, much research has been devoted to chemicals that can extract metals with little effect on the soil structure.

Chelating agents. Chelating agents (chelates) form stable complexes with metals. The strength of the resulting complex depends on the number of rings or sites, attachment on the coordination compound, and the type of metal species present. Chelating agents that attach at only one point are called monodentate ligands, while those with more than one attachment site are referred to as multidentate ligands. When contacted with metals bound to soil particles, the functional groups or sites on the chelate bind with the metals sorbed to the soil surfaces. Since the metal will usually have a greater affinity for chelate site attachment than soil attachment, a net solubilization of the metal species occurs. EDTA is an example of a multidentate ligand that has six sites for attachment (Figure 1). It can form up to six complexes with metal ions on its four acetate groups and two nitrogen atoms that hold free electron pairs (Snoeyink and Jenkins 1980). In addition to EDTA, other typical chelating agents used for metal extraction and soil washing include (NTA), diethylenetriaminepentaacetic acid (DTPA), and citric acid.

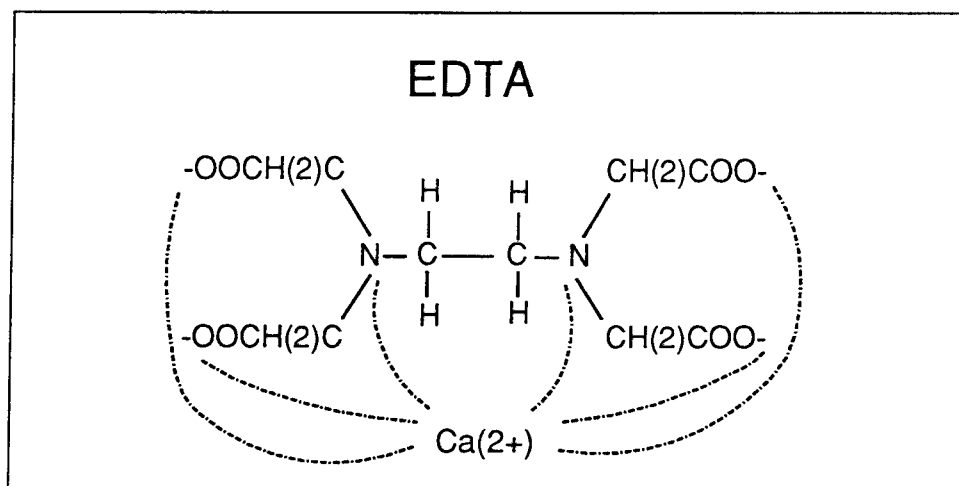


Figure 1. EDTA site attachment (after Snoeyink and Jenkins 1980)

Properties affecting extraction. Some properties of soil and contaminants, specifically metals, can significantly affect the ability of an extracting agent to leach metals or other contaminants from soil. Among the more important properties are cation exchange capacity (CEC), pH, total organic carbon (TOC), and soil chemical phase groups.

Cation exchange capacity. CEC refers to the number of exchange sites within a soil that can sorb cations (Pierzynski, Sims, and Vance 1994). The number of exchange sites on clay soil particles can remain constant or fluctuate with changes in pH. Stable sites result from natural electrostatic forces within soil, while pH-dependent sites typically increase with an increase in pH (Brady 1974). Most trivalent metals such as aluminum (Al^{3+}) generally have a greater affinity for these sorption sites than divalent and monovalent cations (Brady 1974). In most cases, soils with a larger fraction of humus or organic material will have a larger number of cation exchange sites. Table 1 outlines some of the major types of soils in the United States and their respective CEC values. The values indicate that sand particles have the smallest CEC, while clay and clay loam particles have the greatest CEC. The table also reveals that CEC can widely vary within a soil type as evidenced by the two soils characterized as clay and clay loam. Soils can also have an anionic exchange capacity (AEC) if the charges on the soil particles are positive as opposed to negative.

Table 1 CEC of Major United States Soils		
Soil Description	Soil Type	CEC, meq/100 g of dry soil
Sand	Plainfield, WI	3.5
Sandy Loam	Norfolk	3.0
Sandy Loam	Cecil, SC	5.5
Loam	Hoosic, NJ	11.4
Loam	Dover, NJ	14.0
Silt Loam	Dawes, NE	18.4
Silt Loam	Carrington, MN	18.4
Clay and Clay Loam	Cecil clay, AL	4.8
Clay and Clay Loam	Gleason clay loam, CA	31.5
Note: after Brady (1974).		

pH. The relative acidity or basicity of a soil can either increase or decrease the strength of bonds between soil and trace metals. In acidic soil, most of the binding sites on the soil are dominated by protons. The resulting hydrogen-soil bonds are highly resistant to cation exchange (Brady 1974). On the other hand, the exchangeable sites of soils that are naturally basic are attached to exchangeable ions like Ca^{2+} , Mg^{2+} , and potassium (K^{+}). Basic soils are usually amenable to cation exchange and therefore have a higher CEC. As a result, it is often useful to increase the pH of a soil to increase the rate of cation exchange. This increase can be easily accomplished by tilling a powdered lime ($\text{Ca}(\text{OH})_2$) slurry into the soil (Brady 1974).

Total organic carbon. The amount of TOC within a soil greatly enhances the absorption of metal cations. Organic or humic soil material has an extremely high surface area and therefore has a greater number of exchange sites than other soil particles. These ion functional exchange sites are usually attached to protons; however, increases in pH can result in dissociation of the soil surface site and H^+ , thus freeing sites that are available for adsorption by other cations (Bohn, McNeal, and O'Conner 1985).

Surface area. The total surface area of a soil can affect its sorption of metal contaminants. Smaller clay particles have a much greater surface-to-volume ratio and thus have more area for contact with extraction fluids than do larger sand particles. They also contain higher concentrations of contaminants than the sand particles.

Soil components and solubilities of metal compounds. The extractability of metal ions from soil or the rate of metal extraction is also influenced by the type of soil components, or the negatively charged fractions of the soil that can serve as attachment sites for cationic species (Manahan 1994). For example, metals are most easily removed from soils that contain a high percentage of carbonates, whereas removal of metals from soils with high clay mineral content may be difficult (Bricka, Williford, and Jones 1993). The difference is caused by the relative strength of bonding between metals bound to carbonates versus metals bound to the clay mineral fraction of the soil. Table 2 summarizes the ease of extraction of cationic metals from five soil components.

Table 2
Comparison of Chemical Phase Soil Groups

Chemical Phase Soil Groups	Ease of Metal Removal (Ranking of 1 = easiest rate of removal)
Carbonates	1
Iron and Manganese Oxides and Hydroxides	2
Organic Matter	3
Sulfides	4
Clay Minerals	5
Silicates	Unknown
Note: Bricka, Williford, and Jones (1993); Tuin and Tels (1990a).	

The solubility of metal compounds also plays a critical role in the extractability of metals. For example, nitrates are highly soluble in water; therefore, HNO_3 might be an effective extracting agent. When HNO_3 is applied, H^+ ions displace the metal cations in the soil matrix, resulting in the formation of highly soluble metal-nitrate salts that will remain in solution and will not become reentrained in the soil matrix as a precipitate.

Table 3 lists some common metallic compounds and their solubilities in aqueous solution. This table contains useful information for the screening of potential extracting agents to be used in soil washing applications.

Table 3 Generalizations on Solubilities of Metallic Compounds
Nitrates and acetates are soluble in water; silver acetate, chromium (II) acetate, and mercury (I) acetate are slightly soluble.
Chlorates are soluble in water except potassium chlorate, which is slightly soluble.
Chlorides are soluble except mercury (I), silver, lead, and copper (I) chloride; lead chloride is soluble in hot water.
Sulfates except for strontium, barium and lead sulfate are soluble; calcium sulfate and silver sulfate are slightly soluble.
Carbonates, phosphates, borates, arsenates, and arsenites are insoluble except those of ammonium and the alkali metals.
Sulfides of ammonium and alkali metals are soluble, while other sulfides are not; alkaline earth metal sulfides become hydrolyzed in water.
Hydroxides of sodium, potassium, ammonium, barium, and strontium are soluble, while other hydroxides are not; calcium hydroxide is slightly soluble.
Note: after Nebergall, Schmidt, and Holtzclaw (1976).

Background

Several studies have attempted to optimize the metal extraction process using acids, bases, and chelating agents. These studies have investigated the different types of parameters that might affect metal extraction including soil-to-extracting agent ratio, types and concentrations of extracting agents, and contact time.

Argonne National Laboratories and chelating agents

Dr. Robert Peters of Argonne National Laboratories (Peters and Shem 1991) has done extensive research on the complexation of metals through the use of a variety of chelating agents. In selecting the best chelating agents to use in testing, Peters developed five major selection criteria:

- Reagents that form stable complexes over wide pH range at 1:1 ligand-to-metal molar ratio.
- Low biodegradability of complexing agents and complexes.
- Metal complexes are nonadsorbable.

d. Low environmental harm of chelating agents.

e. Cost-effectiveness.

The agents that best meet these criteria and that have been extensively studied are EDTA, NTA, and DTPA.

The majority of Peters' laboratory testing focused on EDTA and NTA. His experiments used uncontaminated soil spiked with 10,000 ppm Pb and then treated with chelate concentrations of 0.01 M, 0.05 M, and 0.1 M of EDTA and NTA. Other testing parameters used in Peters' experiments include variation of pH and a general contact time of 30 min. Table 4 summarizes the resulting Pb removal efficiencies.

Table 4 Comparison of Pb Removal Rate Using EDTA and NTA			
Chelating Agent	Concentration, M	pH	Percent of Pb Removal
EDTA	0.1	6	61
NTA	0.1	6	4
EDTA	0.1	8	60
NTA	0.1	8	2
EDTA	0.1	10	58
NTA	0.1	10	11
Note: Peters and Shem (1991).			

The data shown in Table 4 reveal that 0.1 M EDTA was much more effective for Pb removal than 0.1 M NTA, regardless of pH. Peters' studies of chelating agents have also led to other observations:

- a. EDTA easily removes Cd.
- b. Solid-to-liquid ratio of 0.11 is optimal for both reagents.
- c. EDTA and Pb reach equilibrium in 1 hr.
- d. NTA and Pb reach equilibrium in 3 hr.
- e. Higher temperatures may speed solubilization of metals.
- f. Cr removal increases with increase in pH.

EDTA and HCl experiments

Tuin and Tels (1990b) also conducted experiments to study the effectiveness of EDTA as a metal-complexing agent. They used a two-stage extraction process in which contaminated soils were contacted with 0.1 N HCl followed by 0.1 M EDTA. The contact time for these experiments was 1.5 hr with a solid-to-liquid ratio of 0.05 as compared to Peters observation of 0.11 (weight/weight basis). Table 5 summarizes their results of Pb extraction from clay soils at two industrial waste sites. The percent removal of Extraction 2 represents the amount of metal extracted from the soil using the quantity of metal remaining in the soil after Extraction 1.

Table 5 Metal Extraction From Contaminated Industrial Waste Sites			
Soil Location	Target Metal	Extraction 1 Percent Removal 0.1N HCl	Extraction 2 Percent Removal 0.1M EDTA
Sophia	Cd	50	13
	Cr	16	--
	Pb	52	61
Melchior	Cd	50	17
	Cr	5	3
	Pb	53	72
Note: Tuin and Tels (1990b).			

The results show that a sequential extraction using two solutions generally improved Pb, Cd, and Cr removal in both soils tested.

Comparative complexation tests

Elliott and Brown (1989) have also conducted comparative tests to evaluate the extraction capabilities of EDTA and NTA. Their study focused on the percent removal efficiency of the two chelating agents when mixed with a soil contaminated with 211,000 mg/kg Pb at varying pH.

Using a solid-to-liquid ratio of 0.04 (weight/weight basis) and contact time of 5 hr, these results (Table 6), like the results from Peter's work, show that Pb removal using EDTA was greater than removal using NTA. EDTA was generally a more effective extracting agent than NTA because the stability constant of Pb-EDTA²⁻ (18.0) is much greater than that of Pb-NTA⁻ (11.4). Pb removal efficiency of EDTA ranged from 34 percent at pH = 10 and a concentration of 0.02 M to 95 percent at pH = 4 and a concentration of 0.08 M. Pb extraction using NTA ranged from 11 percent at pH = 12 and a concentration of 0.01 M to 62 percent at pH = 10 and a concentration of 0.06 M.

Table 6
Percent Removal of Pb From Contaminated Soil

Chelating Agent	Concentration, M	pH	Percent Pb Removal
EDTA	0.02	4	45
EDTA	0.02	6	45
EDTA	0.02	8	38
EDTA	0.02	10	34
EDTA	0.02	12	38
EDTA	0.04	4	--
EDTA	0.04	6	68
EDTA	0.04	8	64
EDTA	0.04	10	65
EDTA	0.04	12	60
EDTA	0.06	4	89
EDTA	0.06	6	81
EDTA	0.06	8	75
EDTA	0.06	10	67
EDTA	0.06	12	70
EDTA	0.08	4	95
EDTA	0.08	6	82
EDTA	0.08	8	76
EDTA	0.08	10	67
EDTA	0.08	12	65
NTA	0.01	4	--
NTA	0.01	6	22
NTA	0.01	8	20
NTA	0.01	10	15
NTA	0.01	12	11
NTA	0.02	4	--
NTA	0.02	6	35
NTA	0.02	8	28
NTA	0.02	10	25
NTA	0.02	12	20
NTA	0.04	4	--
NTA	0.04	6	59
NTA	0.04	8	53
NTA	0.04	10	47
NTA	0.04	12	30
(Continued)			

Table 6 (Concluded)			
Chelating Agent	Concentration, M	pH	Percent Pb Removal
NTA	0.06	4	--
NTA	0.06	6	40
NTA	0.06	8	45
NTA	0.06	10	62
NTA	0.06	12	42
NTA	0.08	4	--
NTA	0.08	6	27
NTA	0.08	8	34
NTA	0.08	10	60
NTA	0.08	12	46
Note: Elliott and Brown (1989), Elliott et al. (1989).			

A study by Norvell (1984) compared the metal extraction efficiency of EDTA, NTA, and DTPA. Using a solid-to-liquid ratio of 0.2 (weight/weight basis), the extraction tests were performed on soils contaminated with a variety of trace metals. Analyzing the extracting agents for each metal, Norvell ranked the extraction effectiveness of each chelating agent versus the target metal. His results are shown in Table 7.

Table 7 Effectiveness of EDTA, NTA, and DTPA Versus Target Metals		
Target Metal	Expected Rank	Observed Rank
Al	DTPA > NTA > EDTA	NTA > DTPA > EDTA
Zn	DTPA > EDTA > NTA	DTPA = EDTA = NTA
Cu	DTPA > EDTA > NTA	DTPA = EDTA = NTA
Cd	DTPA > EDTA > NTA	EDTA = DTPA = NTA
Note: Norvell (1984).		

Table 7 indicates that the theoretical order of the chelating agents by effectiveness were contradicted by the observed removal. EDTA, NTA, and DTPA were equally effective in removing Zn, Cu, and Cd, while NTA was more effective in removing Al.

Acid extraction comparison of HNO₃ and HCl

A number of studies have been conducted to determine the metal extraction efficiency using only strong acids. One such study was performed by Mortazavi, Volchek, and Whittaker (1992) on a soil contaminated with various metals. The soil and extracting agent were mixed for 3.5 hr. Results from this study are in Table 8.

Table 8 Extraction Test Using HCl and HNO₃				
Acid, 0.1M	Percent Removal of Cd	Percent Removal of Cu	Percent Removal of Zn	Percent Removal of Pb
HCl	54	23	80	33
HNO ₃	39	58	50	66
Note: Mortazavi, Volchek, and Whitaker (1992).				

These results show that both HCl and HNO₃ are fairly effective extracting agents depending on the metals targeted for removal. Table 8 also illustrates the importance of the solubility of the resulting metallic salts. According to Table 3, Cu (I)-chlorides and Pb-chlorides are insoluble in water, whereas Cu-nitrates and Pb-nitrates are soluble in water. Thus, it is expected that HNO₃ will be a better extracting agent than HCl for the removal of both of these metals. The results shown in Table 8 validate these findings since the removal percentages of Cu and Pb were higher using HNO₃ as the extracting agent than HCl. Table 8 also indicates that HCl had a better removal rate for Cd and Zn than HNO₃.

Neuhauser and Hartenstein (1980) also studied the metal extraction effectiveness of HCl on anaerobic sludges. In their experiment, a solid-to-liquid ratio of 0.033 (weight/ weight basis) was used with a mixing time of 1 hr. Their results (Table 9) indicate that, in general, HCl was effective at removing metals from anaerobic sludge. In particular, 1 M HCl was a better extracting agent than 0.1 M HCl for all metals tested, although nickel and cadmium removal percentages were not appreciably different.

Other laboratory tests

A variety of other chemical compounds have been evaluated as metal extracting agents. The U.S. Bureau of Mines has successfully used fluorosilicic acid to leach Pb from spent battery casings (99-percent removal) (Royer, Selvakumar, and Gaire 1992). Strong bases like sodium hydroxide (NaOH) have also been investigated for their extraction potential as a result of the amphoteric nature of metals in soil that are soluble at both high and low pH values. Assink (1985) asserted that NaOH

Table 9
Percentage of Total Metals Extracted From Anaerobic Sludge

Metal	Concentration, ppm	Percent Removal 1M, HCl	Percent Removal 0.1M, HCl
Cadmium (Cd)	96	67.9	65.3
Copper (Cu)	973	47.8	15.9
Nickel (Ni)	814	26.6	21.1
Lead (Pb)	735	66.0	37.4
Zinc (Zn)	4,202	93.0	71.3
Chromium (Cr)	1,949	55.6	26.0
Note: Neuhauser and Hartenstein (1980).			

dissolves or disperses metal contaminants during extraction, especially those contaminants in the clay or humus soil fractions.

Pilot-Scale Mobile Soil Washing Operations

Recognizing the potential for implementing soil washing technologies in the field, many private industries have tried to develop soil washing systems for remediating soils contaminated with hazardous wastes. Some of these systems focus exclusively on the removal of organic contaminants, while others use soil washing technologies to remove both organics and trace metals. In fact, most of these systems have been demonstrated at Superfund sites through the USEPA's Superfund Innovative Technology Evaluation (SITE) program. Some of the more effective soil washing units are profiled in the following sections along with a summary of their treatment effectiveness.

BioTrol soil washing system

The BioTrol soil washing process is one of the soil washing treatment technologies that has been evaluated by USEPA through a SITE demonstration. As shown in Figure 2, the BioTrol system is composed of several processes that either separate particles based on their size and density or chemically extract contaminants from soil. In this process, contaminated soil is first mixed with water in a trommel to form a slurry. The soil is then sent to a countercurrent attrition/classification circuit. This circuit produces three effluents including fine oversized material, washed soil, and wasted process water containing suspended fine particles. The washed soil represents the end product of the system, while the wasted process water suspension is sent to a thickener to dewater the fine particles and solidify them into a particle cake. Both the filter cake and the leftover fine particles and oversized material must be properly treated or disposed (Stinson, Skovronek, and Ellis 1992).

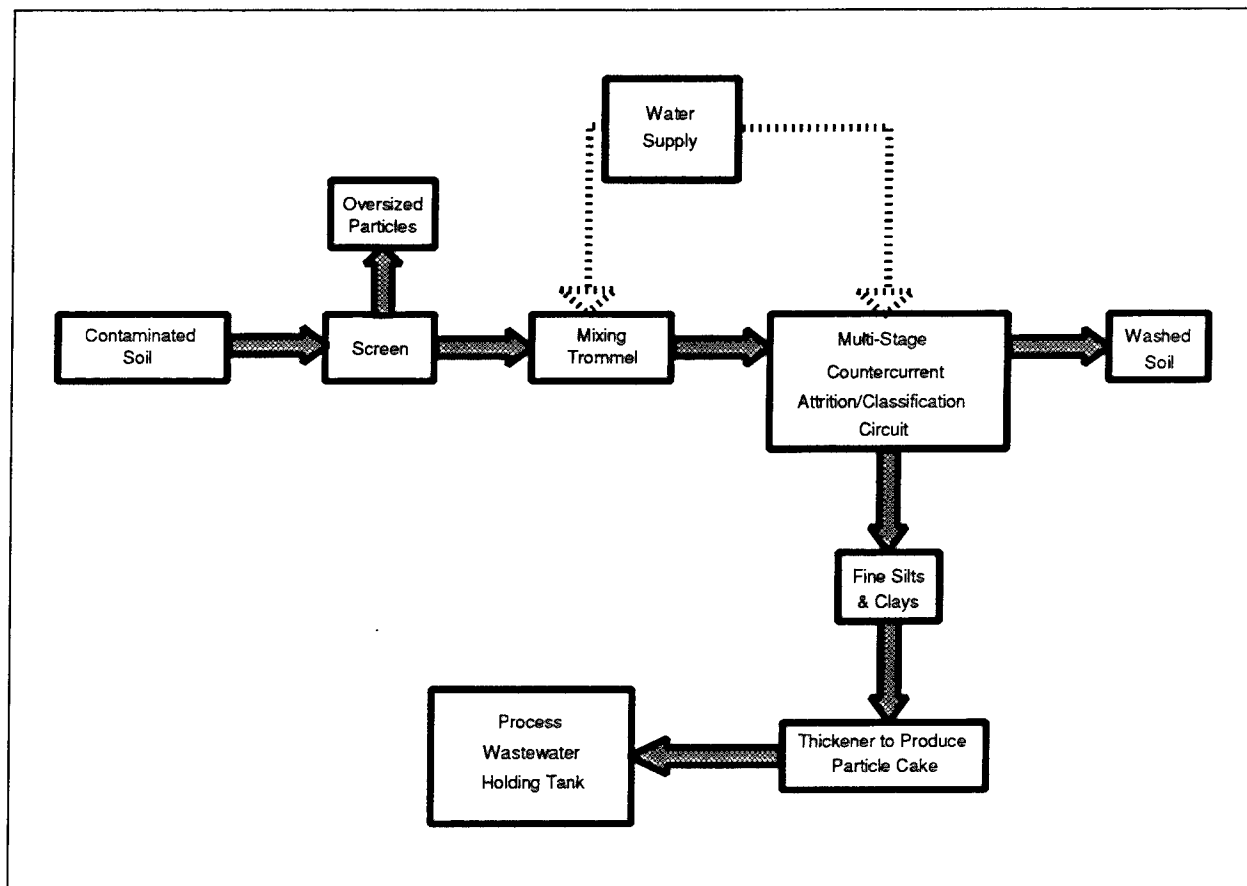


Figure 2. BioTrol soil washing process (after Stinson, Skovronek, and Ellis 1992)

The BioTrol process was used in a SITE demonstration at the MacGillis and Gibbs Superfund site in New Brighton, MN. This site formerly housed a wood-preserving facility and was heavily contaminated with pentachlorophenol (PCP), polynuclear aromatic hydrocarbons (PAHs), and trace amounts of Cr (Stinson, Skovronek, and Ellis 1992).

Two test runs were completed to determine the effectiveness of the BioTrol process. The first test run produced an 89-percent reduction of PCP, an 80-percent reduction of carcinogenic PAHs, and a 48-percent reduction of Cr. The second test run produced slightly higher reduction percentages: 87-percent reduction of PCP, 87-percent reduction of carcinogenic PAHs, and 64-percent reduction of Cr (Stinson, Skovronek, and Ellis 1992).

Cognis/Bescorp Terramet soil washing plant

Another promising soil washing system has been developed through the collaborative efforts of two companies: Cognis, Inc., of Santa Rosa, CA, and Bescorp, Inc., of Fairbanks, AK. As with the BioTrol system, the operation of the Cognis/Bescorp Terramet plant is divided into a physical separation phase and a chemical

extraction phase. Figure 3 shows the contaminated soil feeding into a trommel, which agitates the soil to remove oversized particles and to break up any agglomerated soil lumps. The oversized material is sent to an ordnance-removal conveyor, while the soil fraction that passed through the trommel is sent to a separation chamber to be further classified into sand and fines fractions. The sand and fines fractions are separately sent through a four-stage countercurrent leaching process to remove metal contaminants from the soil. The washed soils are dewatered and then recombined with the oversized fraction. The mixture is neutralized and returned to the original site.

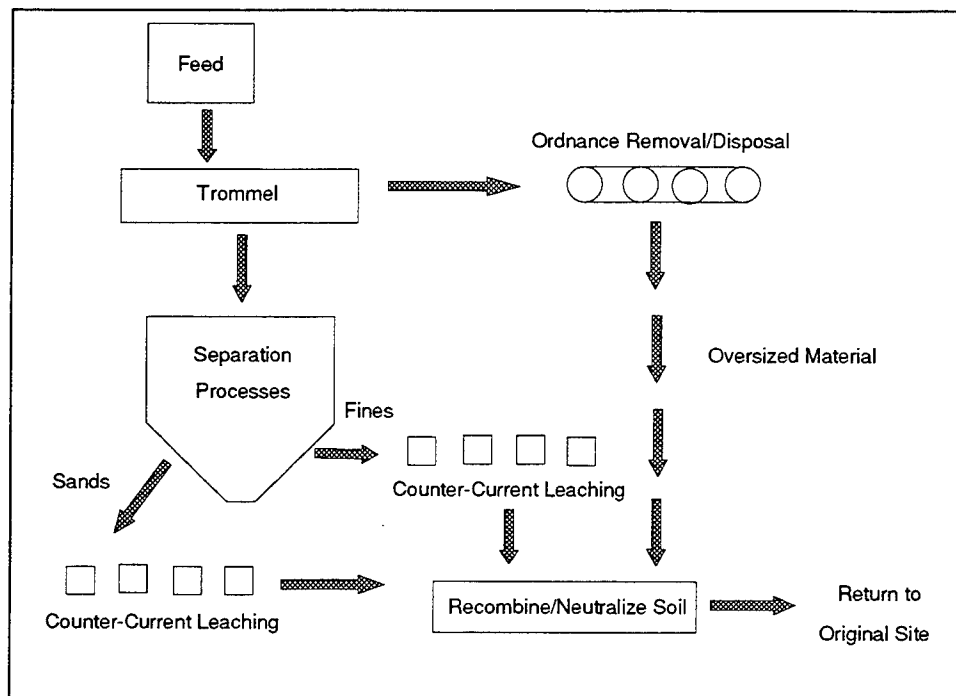


Figure 3. Cognis/Bescorp Terramet soil washing plant (after COGNIS 1993)

Since 1993, the Cognis/Bescorp Terramet Soil Washing Plant has been used to remediate contaminated soil from Site F of the Twin Cities Army Ammunition Plant (TCAAP) in Arden Hills, MN. Most of the contamination at this site resulted from open burning, ammunitions burial, and open detonation of explosives. Remediation of the site has been especially challenging since trace metal contamination had to be restored to naturally occurring background levels. However, the Cognis/Bescorp system has been able to meet all of the cleanup criteria as mandated by USEPA and the Minnesota Pollution Control Agency for the majority of the soil processed. Some of the cleanup results are summarized in Table 10. These results indicate that the Cognis/Bescorp system has been highly effective at remediating soils contaminated with trace metals.

Table 10
Terramet Acceptance Period Results at TCAAP

Metal	Cleanup Goal, ppm	Sampling Period 1	Sampling Period 2	Sampling Period 3	Sampling Period 4	Sampling Period 5	Sampling Period 6
Antimony	4	<1	<1	<1	< 1	<1	<1
Cadmium	4	0.8	1.8	<0.02	3.0	0.2	1.5
Chromium	100	3.5	0.6	2.6	6.0	5.0	5.0
Copper	80	23.7	12.6	9.8	12.7	16.1	11.3
Lead	300	19	60	30	<60	<60	38
Mercury	0.3	<0.02	0.04	0.03	<0.02	<0.02	0.3
Nickel	45	8.9	6.2	4.6	5.4	6	7.8
Silver	5	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

Note: after COGNIS, Inc. (1993).

2 Objective and Scope of Work

The effectiveness of soil washing depends largely on three conditions: the distribution and concentration of contaminant, the type of soil, and the type of extracting agent. The role that each of these conditions plays in the effectiveness of soil washing must be evaluated before attempting a full-scale cleanup of the site. As a result, potential treatments must be fully evaluated at bench or pilot scale using a system similar to the type of system that will be used in the field.

The main objective of this research was to design and develop a pilot-scale continuous-flow countercurrent soil washing unit that could effectively be used to evaluate the ability of a similar, but full-scale system to remove trace metals from contaminated soils at Federal facilities. However, this particular study focuses only on the investigation of operating parameters for such a pilot-scale system.

A pilot-scale continuous-flow countercurrent metal extraction system has been constructed and will be fully evaluated as a potential model of a full-scale soil washing system. Efficient and effective operation of the countercurrent metal extraction system requires optimization of several operating parameters. Several batch studies were carried out to determine these operating parameters.

The scope of work of this research is outlined below:

- a. Construct the pilot-scale continuous-flow countercurrent metal extraction system.
- b. Perform a solid-to-liquid ratio batch test to determine the optimal ratio between contaminated soil and extracting agent for the removal of metal contaminants.
- c. Perform an extractant-effectiveness batch test to determine the most effective extracting agents for metals in contaminated soils.
- d. Perform a steady-state batch test to determine the reaction time for soil and extracting agent to reach chemical steady state.

3 Materials and Methods

This section outlines the scope of work for the project, the design of the pilot-scale countercurrent metal extraction system, and the test methods for the batch experiments.

Figure 4 presents the scope of work for the project. This report only covers the data analysis for the batch experiments. Details of the results of the operation of the pilot-scale extraction system will be presented in a separate report.

Design and construction of the countercurrent metal extraction system was completed in 3 months. Figure 5 gives a detailed schematic of the pilot-scale system, which consists of four identical sets of reactor and clarifiers that were specially constructed by Ace Glass, Inc., of Vineland, NJ. Nomenclature for Figure 5 is as follows: S = sampling valve, V = pinch valve, M = mixer, T = tank, P = pump, C = clarifier, and R = reactor.

System Flow Regulation

System flow is regulated through the use of two identical digitalized console pump drives supplied by Cole-Parmer Instrument Company (Model Number G-07523-30). These drives, each with a maximum flow rate of 380 ml/minute, hold four Masterflex Easy-load L/S pumpheads (Model 751802). One drive is used for controlling the flow of the initial soil slurry and fresh extracting agent solution, while the other drive pumps the underflow slurries from clarifiers in each of the four stages to reactors in the previous stage, thus achieving countercurrent flow.

Reactor Design

Each reactor (Model Number QC617-1) holds approximately 2 l of solution and contains four baffles that are designed to ensure that complete mixing is achieved. As shown in Figure 6, the reactors are cylindrical in shape with a height of 12 in. and a base diameter of 5 in. They contain two outlets on the side of the vessel. The three-fourths inch overflow outlet is located approximately 1 in. from the top of the

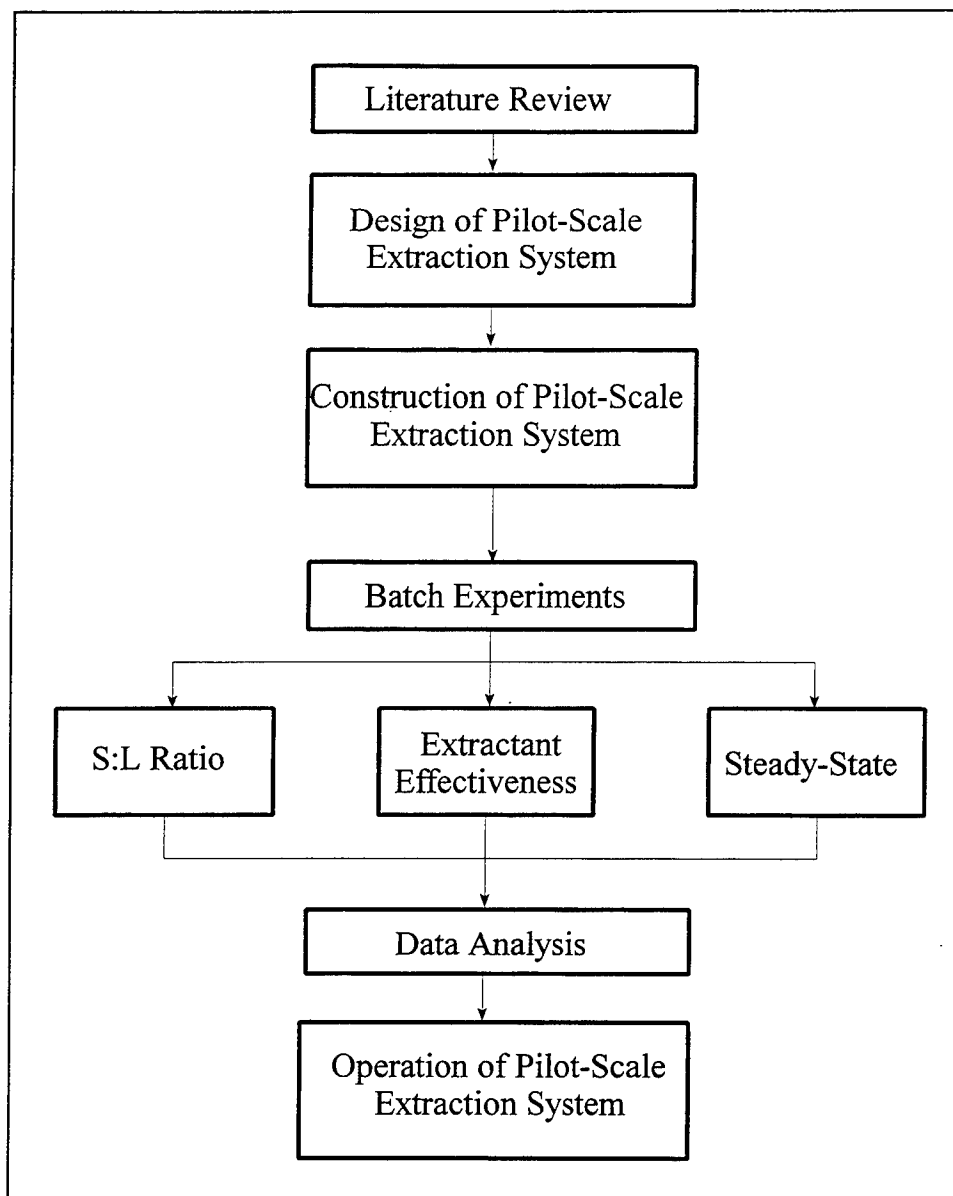


Figure 4. Scope of Work

vessel while the three-fourths inch underflow outlet is placed 1 in. above the base and makes a 45-deg angle with the base of the vessel. Each reactor is equipped with a glass reaction flask head (Model Number QC617-1) that contains three 1-in. ports or openings. Standard clamps (Model Number 6496-10) are used to hold the reactor and reaction flask head together.

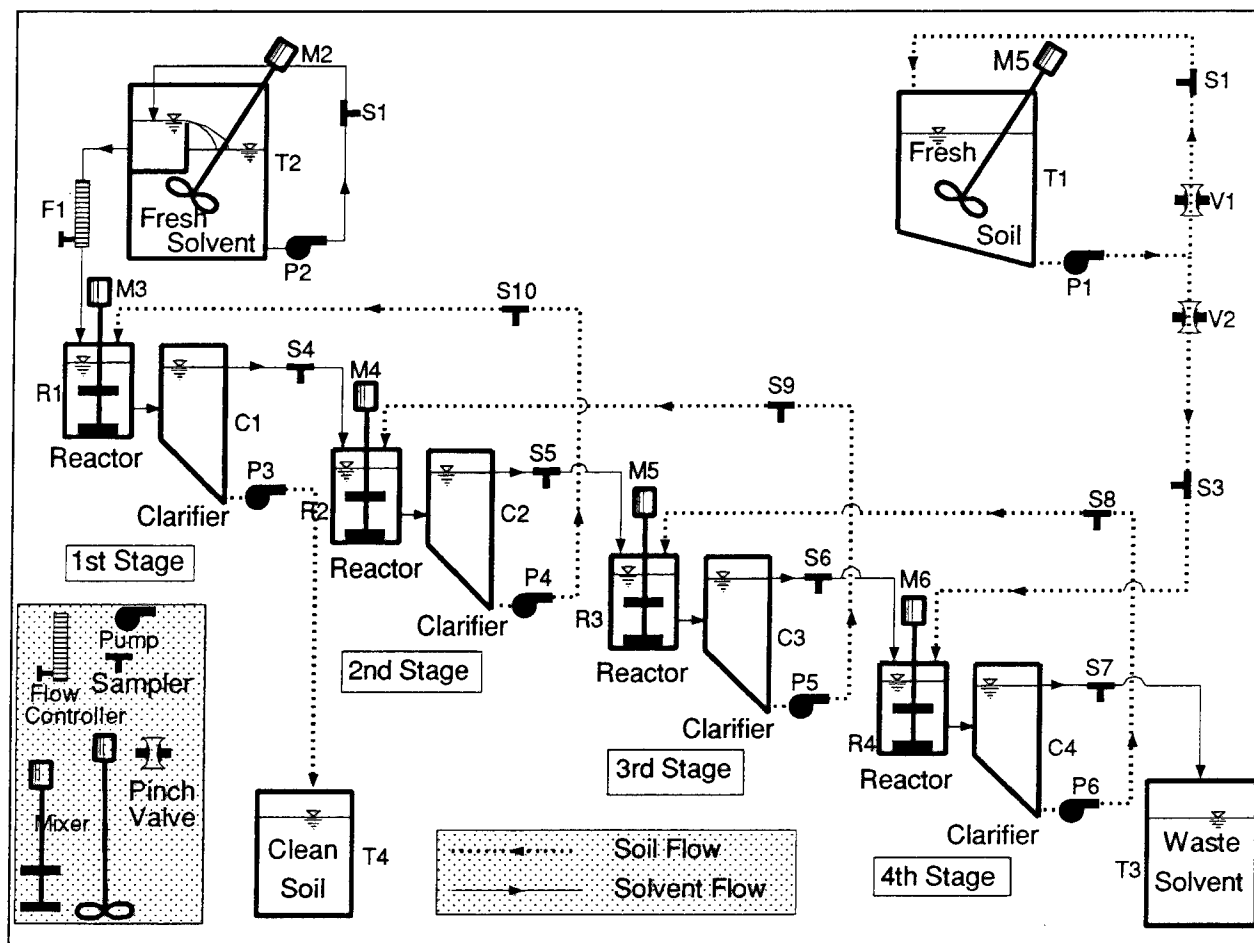


Figure 5. Schematic of pilot-scale continuous-flow countercurrent metal extraction system

Clarifier Design

Each clarifier (Model Number QC617-3) holds approximately 2 l of solution and is equipped with two three-fourths inch inlets and two three-fourths inch outlets as shown in Figure 7. The two inlets are connected to the reactor using three-fourths inch Tygon tubing. The clarifiers are cylindrical in shape with a 45-deg angled bottom and have the following dimensions: heights from base outlet to top of vessel and from top of angle to top of vessel are 15.5 and 10.5 in., respectively. Its base diameter is 5 in. The angled bottom allows solids to more easily move the bottom outlet of the vessel, while the less turbid extracting fluid remains near the top of the clarifier. Multiring rubber stoppers (150-mm top diameter, 138-mm bottom diameter) serve as tops for the clarifiers.

Mixing Apparatuses

Each of the four reactors is furnished with a Lightnin' L1U08F Labmaster variable speed mixer with 30-in. shaft (Model 310 Impeller) that delivers a maximum mixing speed of 1,800 rpm. The mixers are mounted with their mixing shafts entering the center hole of the reactor vessel top. The mixers ensure adequate contact between the incoming soil slurry and extracting agent.

A 15-gal Nalgene tank is used to store the soil slurry. The slurry is mixed using a Lightnin' Model XJ-30VM variable speed mixer with a 9-in. diameter impeller. The extracting agent solution is prepared in a 50-gal Nalgene tank and mixed using a Lightnin' Model CS-LB566 single-speed mixer.

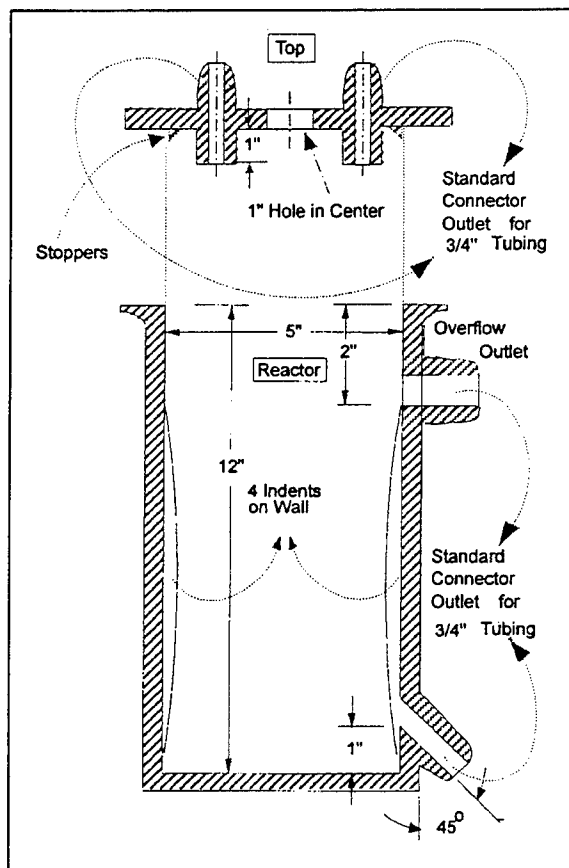


Figure 6. Reactor vessel

Selection of Test Soils

A wide variety of soils from across the country were initially selected for batch experiments. One of the criteria for selection focused on the predominant soil type: sand, silt, or clay. Another key selection criteria centered on the type of metal contaminant found in the soil matrix. The selected soils, their location, soil type, and predominant contaminant are listed in Table 11.

Selection of Extraction Agents

Based on the review of literature, a list of potential metal extracting agents was compiled. The final list of agents included a variety of acids and chelating agents that had shown promise for the removal of metals from soil in previous research experiments. Two of the extracting agents evaluated, NTA and fluorosilicic acid, were not selected for use in the countercurrent metal extraction system because

NTA is a suspected carcinogen and fluorosilicic acid aggressively destroys the matrix of the soil. Other selected extracting agents included HNO_3 , HCl , citric acid, EDTA, DTPA, and NaOH . Three different concentrations of 0.01 M, 0.05 M, 0.1 M were tested to evaluate the relationship between metal extraction and extracting agent concentration.

Characterization Methods

Laboratory tests used to characterize the soils are outlined in Table 12. They are briefly discussed in the following paragraphs.

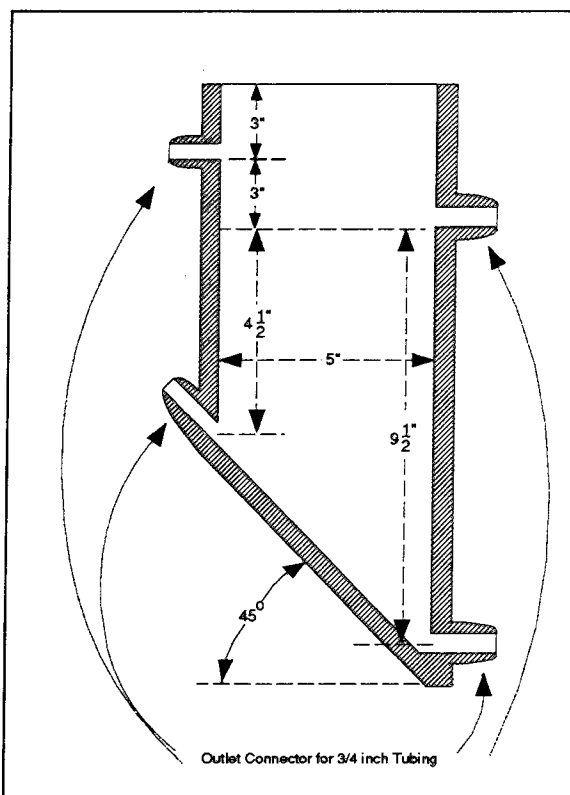


Figure 7. Clarifier vessel

Table 11 List of Soils Selected for Batch Testing			
Site	Location	Soil Type	Contaminant
LAAP Site 1	Shreveport, LA	Clay/Silt	Chromium
LAAP Site 2	Shreveport, LA	Clay/Silt	Chromium
Fort Ord	Monterey, CA	Sand	Lead
SE Fort Site 12	Southeastern U.S.	Sand	Lead
SE Fort Site 10	Southeastern U.S.	Clay	Lead
SE Fort Sites 5-8	Southeastern U.S.	Clay/Sand	Lead
Umatilla Army Depot	Hermiston, OR	Sand	Lead, Cadmium
WES Spiked Soil	Vicksburg, MS	Clay/Sand	Multiple Metals

pH

To measure pH, each of the soils was classified as either calcareous (containing calcium or calcium carbonate) or noncalcareous according to geological soil surveys. For noncalcareous soils, a 20-g soil sample was added to a 50-ml beaker and mixed with 20 ml of deionized, distilled water (DDI) for approximately 30 min. After 1 hr

Table 12
Soil Characterization Methods

Soil Characterization Test	Method Used
pH	USEPA Method 9045
Moisture Analysis	ASTM Method D2216-92
Total Organic Carbon	USEPA Method 9060A
Cation Exchange Capacity	USEPA 9081
Total Metals Content	USEPA Method 3050, EPA Method 3051
TCLP	USEPA SW-846 Chapter 7, Section 4
Particle Size Distribution	Tan (1991)

without agitation, the pH of the slurry was measured using a Beckman Model 45 pH meter. For calcareous soils, a 20-g soil sample was added to a 50-ml beaker and mixed with 20 ml of 0.01 M CaCl_2 for 30 min. After 30 min without agitation, the pH of the slurry was measured using a Beckman Model 45 pH meter (USEPA Method 9045).

Moisture analysis

To measure the total moisture content of the soil, a 20-g sample was placed in a preweighed aluminum tin, and the total mass of the specimen and tin was recorded. The sample was then placed in an oven at $110 \pm 5^\circ\text{C}$ for 24 hr. After removal from the oven, the samples were weighed, and a moisture content was determined. The samples were then returned to the oven for another 24-hr drying period. The samples were again removed from the oven and weighed to ensure complete moisture evaporation, and the overall moisture content of the sample was determined (ASTM D2216-92) (American Society of Testing and Materials (ASTM) 1992).

Total organic carbon

To measure the TOC of each soil, a small amount of the soil was homogenized, diluted with carbon-filtered water, and oven-dried at 105°C for 24 hr. A 0.2-g portion of each sample was placed in a beaker containing DDI water. The slurry was boiled for 30 min and then analyzed for TOC using an O/I Model 700 Total Organic Carbon analyzer.

Cation exchange capacity

To measure the CEC of each soil, 4 g of sample was placed in a 50-ml centrifuge tube containing 33 ml of 1.0 N sodium acetate. The sample was shaken for 5 min

and centrifuged until no visible solids remained in the supernatant liquid. The liquid was decanted, and another 33 ml of 1.0 N sodium acetate was added. This procedure was repeated two more times. Subsequently, 33 ml of 99-percent isopropyl alcohol was added to the centrifuge tube and shaken for 5 min. The sample was centrifuged, and the clear liquid was decanted. This procedure was repeated two more times. Finally, 33 ml of 1.0 N ammonium acetate was added to each tube and shaken for 5 min. After centrifugation, the supernatant was added to a 100-ml volumetric flask. This step was repeated two more times. The combined supernatant was diluted to 100-ml with ammonium acetate (USEPA 9081). Sodium concentration and subsequent CEC were determined by inductively coupled plasma spectroscopy and atomic absorption spectrophotometry (AAS).

Total metals content (soil digestion)

To determine the total metals content of the soil, a sample from each of the selected soils was thoroughly riffled and mixed to ensure homogeneity. Using the block digestion USEPA Method 3050, approximately 1 to 2 g of each soil sample was placed in a cylindrical, rounded-bottom beaker containing 10 ml of 1:1 HNO₃. The beaker was heated to 95 °C and allowed to reflux for 15 min without boiling. After cooling, another 5 ml of concentrated HNO₃ was added to each beaker until oxidation was complete. Two milliliters of DDI water and 3 ml of 30-percent hydrogen peroxide (H₂O₂) were then added to each beaker to oxidize the organic fraction of the soil. The final sample was filtered using Whatman No. 41 filter paper and diluted to 100 ml using DDI water in a 125-ml Nalgene high density polyethylene (HDPE) bottle.

For most metals analyses, an aliquot of 10 ml of sample was prepared for AAS reading. Some samples contained higher metal concentrations that exceeded the calibration range of the instrument; these samples were appropriately diluted. To ensure analytical accuracy, several quality control procedures were implemented. Duplicates and samples spiked with a known concentration of metal were run on every twentieth sample and had to be within ±30 percent of the original sample concentration. Additionally, standards of known metal concentration were run periodically and were required to have ±20-percent accuracy.

Toxicity characteristics leaching procedure

To determine the concentration of leachable metals as defined by USEPA, a TCLP test was run in triplicate on each soil sample. Using a 5-g soil sample and 96.5 ml of DDI water in a 400-ml beaker, the pH of the slurry was recorded to determine the type of extraction fluid to be used. If the pH was less than 5.0, then extraction fluid No. 1 (5.7 ml acetic acid per liter, 64.3 ml of 1.0 N NaOH per liter) was used. If the pH was greater than 5.0, then extraction fluid No. 2 (5.7 ml acetic acid per liter) was used. Using a 20:1 liquid-to-solid ratio, 40 g of soil and 800 ml of extraction fluid were placed in a 1-ℓ Nalgene HDPE bottle and tumbled for 18 ± 2 hr at 30 ± 2 rpm. After tumbling was complete, the final pH of the samples was measured, and the samples were filtered using Whatman GF/F filters and glass

Millipore filtering apparatuses. The filtered samples were analyzed for metals content using AAS (SW-846 Sect. 7.4) (USEPA 1986).

Particle size distribution

A particle size distribution analysis was conducted to determine the percent content of sand, silt, and clay of each of the selected soils. Fifty grams (dry weight) of soil sample was mixed with DDI and 10 ml of sodium hexametaphosphate (40 g to 1 l of DDI water) in a kitchen blender. After mixing, the solution was poured into an ASTM-approved soil-testing cylinder and diluted to the top mark of the cylinder with DDI water (ASTM 1992). The solution was agitated with a plunger, and a hydrometer was immediately placed into the soil-testing cylinder. Two readings were taken on the hydrometer: one after 40 sec and another after 2 hr, with temperatures recorded at these time intervals. The percent sand, silt, and clay fractions of each soil were subsequently determined (Tan 1991).

Batch Studies

Batch experiments were performed using some or all of the selected soils and extracting agents to determine the operational parameters of the countercurrent metal extraction system. A brief review of each of the batch test procedures is given below. A more detailed description of the procedures can be found in Appendix A.

Solid-to-liquid ratio test

To determine the optimal ratio between soil and extracting agent, two soils (one clay and one sand) and two extracting agents (one strong acid and one chelating agent) were selected. Three samples weighing 15, 60, and 150 g (dry weight) of each of the selected soils were prepared. Each soil sample was placed in a 500-ml Nalgene HDPE bottle with approximately 300 ml of extracting agent to yield the following solid-to-liquid ratios: 0.05, 0.2, and 0.5. The bottles were tumbled for 24 hr at 18 ± 2 rpm. After removal from the tumbling apparatus, the samples were filtered using Millipore Type HA 0.45 μm filter paper and Millipore Sterifil Aseptic Filtration Systems. The filtered liquid was analyzed for metals content using AAS. After determining which solid-to-liquid ratio was optimal based on the concentration of metals in the filtrate, the test process was repeated using ratios that were closer to the initially selected optimal ratio and using longer contact times (up to 60 hr). This second test was used to verify the optimal solid-to-liquid ratio found in the first test.

Extractant effectiveness test

Using the optimal solid-to-liquid ratio found in the previous batch test, all of the selected soils and extracting agents identified in the literature review that were most

effective for removing metals from soil were tested. Soil samples weighing 5 g were mixed with an appropriate volume of extracting agent. These mixtures were tumbled for 30 hr, as established in the literature review and in the previous batch experiment, at 18 ± 2 rpm after which 50 to 75 ml of extracting agent was filtered. Millipore Type HA $0.45 \mu\text{m}$ filters and Millipore Aseptic Filtration Systems were used to complete most of the filtration process. Alternatively, some samples were centrifuged to achieve separation of liquid and solid. Separation by centrifugation was carried out by placing a portion of the slurried sample in a 50-ml Oak Ridge PCDD centrifuge tube and centrifuging it for 15 to 20 min at 15,000 rpm using a Sorvall Superspeed Model SS-3 centrifuge. No appreciable difference in dissolved metal concentration was found in the liquid separated from the soil using filtration versus centrifugation. Analysis of metals content was performed using AAS.

Equilibrium test

An equilibrium test was initiated to determine the length of time needed for the soil and extracting agent to reach chemical equilibrium. Only four of the eight selected soils and four of the eight selected extracting agents were tested. Samples of 45 g (dry weight) were mixed with an appropriate volume of extracting agent (depending on optimal solid-to-liquid ratio) in a 1-l Nalgene HDPE bottle. The sample bottles were tumbled at 18 ± 2 rpm for 30 hr. During this period, 12- to 15-ml samples were drawn at the following time intervals: 0.5, 1, 2, 3, 5, 7, 10 hr, and every 2 hr until completion of the 30-hr cycle. The samples were filtered using a Terumo 10-cc luer lock-tip disposable syringe equipped with Gelman 25-mm $0.45 \mu\text{m}$ DM Metrical membrane filters. The filtered solution was analyzed for metals content using AAS.

Methods of Statistical Analysis of Data

Inferences made by inspection of graphs and raw data from the batch studies were supported through statistical analysis. Multiple comparisons of data were completed using analysis of variance. Both the Waller-Duncan K-ratio T test and the Duncan's Multiple Range tests were performed using SAS statistical software to investigate differences in the sets of data.

Examples of the Waller-Duncan K-ratio T test and Duncan's Multiple Range tests are shown in Table 13 and discussed below.

First, the raw data are entered into the SAS statistical program as shown in Table 13. In this example, the column headings represent the following: OBS = observation number, SOIL = soil type from which metal is being extracted, EXT = extracting agent, CONC = concentration of extracting agent, PB = percent of Pb extracted from the soil, CD = percent of Cd extracted from the soil, CR = percent of Cr extracted from the soil. Once the data have been entered, the Waller-Duncan K-ratio T-test and Duncan's Multiple Range tests can be run. Each of these tests compares all of the potential differences that might exist between sets of data. For

Table 13**Example Raw Data Entry Into SAS**

OBS	SOIL	EXT	CONC	PB	CD	CR
1	5	A	a	0.0	0.0	20.1
2	5	A	b	0.0	0.0	28.3
3	5	A	c	0.0	0.0	40.8
4	5	B	a	0.0	0.0	15.8
5	5	B	b	0.0	0.0	23.3
6	5	B	c	0.0	0.0	32.6
7	5	C	a	0.0	0.0	9.7
8	5	C	b	0.0	0.0	34.4
9	5	C	c	0.0	0.0	50.1

example, in the raw data set above, there are six separate columns of data. Within Column 2, there are three different soil types identified as 5, 6, and 10 (soil types 6 and 10 are not shown above). Within Column 3, there are three types of extracting agents named A-H (only A, B, and C are shown). Column 4 also has three different concentrations of the extracting agents labeled a, b, and c. Using the percent metal removal data for Cr in Column 7, the multiple comparison tests will indicate differences between soil types, extracting agents, and concentrations as they relate to Cr extraction efficiency. The analysis of variance of the example set of data is provided below in Table 14.

Table 14**Example Analysis of Variance Output From SAS**

Analysis of Variance Procedure Class Level Information					
Class		Levels		Values	
Soil		3		10 5 6	
Ext		8		A B C D E F G H	
Conc		3		a b c	
Number of observations in data set = 72					
Analysis of variance procedure					
Dependent variable: Cr					
Source	DF	ANOVA SS	Mean Square	F Value	Pr > F
Soil	2	925.8919	925.8919	1.55	0.2211
Ext	7	21775.7244	3110.8178	10.40	0.0001
Conc	2	4704.4869	2352.2435	7.86	0.0009

This part of the analysis tests for differences between the variables in each class. The probability of error associated with rejecting the null hypothesis is indicated by the value associated with $Pr > F$. For example, Table 14 indicates that the level of confidence of the eight extracting agents (or levels of class EXT) having significantly different Cr removal efficiencies is 99.99 percent. This result indicates that it is likely that the various extraction agents vary in their effectiveness in extracting Cr from the soil. While this analysis indicates that there is a difference between extracts, a Waller-Duncan analysis must be performed to compare these differences.

In the Waller-Duncan analysis shown in Table 15, the similar groups are represented by capital letters A-E located to the left of the means. This grouping analyzes the similarities between the extracting agents or levels of class EXT shown on the right. Reviewing the analysis, extracting agents fluorosilicic acid and citric acid are clearly different from one another and from the rest of the extracting agents. Extracting agents HNO_3 , HCL, NTA, and NaOH are similar as are extracting agents HCL, NTA, NaOH, and EDTA. Extracting agents NTA, NaOH, EDTA, and DTPA are also similar. Some of the extracting agents belong to more than one type of grouping. After determining whether the data sets are significantly different, the best extracting agent can be statistically selected. Since extracting agent fluorosilicic acid is significantly different from the other reagents and since its mean removal efficiency is greatest, fluorosilicic acid is selected as the most effective extracting agent. The same type of analysis is used to investigate differences

Table 15
Example Extracting Agent Comparison Output From SAS

Analysis of Variance Procedure					
Waller-Duncan K-ratio T test for variable: Cr					
Note: This test minimizes the Bayes risk under additive loss and certain other assumptions.					
K-ratio = 100 df = 60 MSE = 299.1018 F = 10.40053					
Critical Value of T = 1.86491					
Minimum Significant Difference = 15.204					
Means with the same letter are not significantly different.					
Waller Grouping			Mean	N	Ext
	A		53.662	9	fluorosilicic acid
	B		37.956	9	citric acid
	C		19.189	9	HNO_3
D	C		16.544	9	HCl
D	C	E	13.300	9	NTA
D	C	E	5.611	9	NaOH
D		E	1.589	9	EDTA
		E	0.500	9	DTPA

between extracting agent concentrations (levels of class CONC) as shown in Table 16.

In this example, the Waller-Duncan grouping indicates a similarity between extracting agent concentrations 0.05M and 0.1M. It also shows significant difference between concentrations 0.01M and 0.05M and concentration 0.1M. Ranking of the means of the concentrations indicates that 0.05M and 0.1M are most effective for removal of the contaminant, while concentration 0.01M is the least effective.

Table 16 Example Concentration Comparison Output From SAS			
Analysis of Variance Procedure			
Waller-Duncan K-ratio T test for variable: Cr			
K-ratio = 100 df = 60 MSE = 299.1018 F = 7.864358			
Critical Value of T = 1.90861			
Minimum Significant Difference = 9.5287			
Means with the same letter are not significantly different.			
Waller Grouping	Mean	N	Conc
A	27.858	24	0.1M
A	19.613	24	0.05M
B	8.146	24	0.01M

4 Results and Discussion

To better analyze the data from the batch experiments, a series of physical and chemical tests were performed on each of the selected soils. These tests included pH, moisture content, TOC, CEC, particle size distribution, total metals content, and TCLP.

After completely characterizing the soils, the batch experiments were completed to determine the optimal operating parameters for the pilot-scale countercurrent metal extraction system. The batch experiments included an optimal solid-to-liquid ratio between the soils and extracting agents, the most effective extracting agents and concentrations, and an appropriate contact time for the soil and extracting agent to reach steady state. Results of both the characterization tests and batch experiments are presented in the following sections.

Results of Soil Characterization

To gain a better understanding of the properties of soils and how these properties might affect the extraction process, several physical and chemical characterization tests were performed. Results of the pH, moisture content, TOC, CEC, and particle size distribution analyses are presented in Table 17. As expected, soils with either a high clay and silt content or elevated TOC levels also registered high CEC values. For example, the WES spiked soil, which contained 18,000 mg/kg TOC and 94.76 percent silt, had the highest CEC value of 15.8 meq/100 g of soil.

However, one of the selected soils contrasted the trend of soils having high values in both TOC and CEC. The SE Fort Site 12 soil recorded a high CEC value, but had the lowest concentration of TOC among the selected soils. The majority of CEC in the sample might be attributed to the large percentage of clay material in the soil.

Chemical characterization tests were also performed to determine the total metals content of the soils and to determine the soils' susceptibility to contaminant leaching. Results from the digestions and TCLP tests conducted on the soils are summarized in Table 18. Most of the values presented in Table 18 represent average concentrations resulting from triplicate and quadruplicate testing.

Table 17
Results of Physical Characterization Tests

Soil	pH	Moisture Content percent	TOC mg/kg	CEC meq/100 g	Particle Size Distribution, percent
Umatilla	9.04	4	910	8.07	Sand: 68.36 Silt: 24.04 Clay: 7.60
Fort Ord	9.06	1	310	10.6	Sand: 88.46 Silt: 8.30 Clay: 3.24
LAAP Site 1	9.51	6	7,800 ^a	6.13	Sand: 77.36 Silt: 15.04 Clay: 7.60
LAAP Site 2	9.64	6	5,200 ^a	8.99	Sand: 73.92 Silt: 19.40 Clay: 6.68
SE Fort Site 10	5.66	14	270	6.54	Sand: 23.98 Silt: 40.42 Clay: 35.60
SE Fort Site 12	4.91	6	230	15.6	Sand: 56.22 Silt: 7.46 Clay: 36.32
SE Fort Sites 5-8	6.50	4	930	3.25	Sand: 71.70 Silt: 10.54 Clay: 17.76
WES Spiked	8.37	26	18,000	15.8	Sand: 5.24 Silt: 94.76 Clay: 0.00

^a Indicates concentration exceeded instrumentation range; values are estimates.

Table 18
Results of Chemical Characterization Tests

Soil	Total Metals Concentration, mg/kg			TCLP Results, mg/l		
	Pb	Cd	Cr	Pb	Cd	Cr
Umatilla	15,969	7	22	1,020 ^a	<1	<1
Fort Ord	4,750	<1	24	104 ^a	<1	<1
LAAP Site 1	19	<1	553	1	<1	3
LAAP Site 2	114	37	1,428	<1	<1	<1
SE Fort Site 10	25,245	<1	24	268 ^a	<1	<1
SE Fort Site 12	21,646	<1	22	796 ^a	<1	<1
SE Fort Sites 5-8	30,347	<1	20	2,677 ^a	<1	<1
WES Spiked	6,831	951	1,992	280 ^a	54 ^a	23 ^a

^a Indicates exceedance of minimum TCLP concentrations.

Each of the selected soils contained high concentrations of at least one metal of concern, and some contained high levels of all three contaminants. Umatilla, Fort Ord, WES spiked, and all of the SE Fort soils had high concentrations of Pb. Both of the LAAP soils and the WES spiked soil contained elevated levels of Cr, and the LAAP Site 2 and WES spiked soils had appreciable levels of Cd.

The minimum regulatory TCLP concentrations for Pb and Cr are 5.0 mg/l and 1.0 mg/l for Cd. Concentrations of metals in soil that exceeded the minimum regulatory concentrations are highlighted in Table 18. All of the soils that contained high initial concentrations of Pb failed the TCLP. However, the two LAAP soils that contained high initial levels of Cr did pass the TCLP test. Presumably, the Cr present in these soils was highly insoluble and in the less toxic trivalent form. The WES spiked soil failed TCLP for all three metals. These failures most likely can be attributed to the fact that the soil was artificially contaminated, and the binding reactions between metal and soil had not occurred for as long a period as for those of the nonspiked soils.

Test results from the TCLP cannot be directly correlated to the physical characterization data already presented. For example, some of the tested soils having high TOC and CEC values or low TOC and CEC values both had high TCLP concentrations. These types of contradictions between soils were also found when trying to correlate the other physical characteristics versus TCLP concentrations.

Results of Batch Tests

Several batch studies were conducted to determine some of the operating conditions needed for running the countercurrent metal extraction system. Results of the solid-to-liquid ratio test, extractant effectiveness test, and equilibrium test are presented in the following sections.

Solid-to-liquid ratio test

Previous studies on metal extraction, as reported in literature, did not reveal a consensus on an optimal solid-to-liquid ratio for achieving the maximum soil washing efficiency of metal-contaminated soils. The solid-to-liquid ratios (S:L) found in literature ranged from a smallest value of 0.03 (Neuhauser and Hartenstein 1980) to a largest value of 0.2 (Norvell 1984).

To effectively test a broad range of S:L ratios, two separate solid-to-liquid ratio tests were performed. The first test used S:L ratios of 0.5, 0.2, and 0.05 for contact periods of 24 and 30 hr. The second test employed smaller S:L ratios ranging from 0.005 to 0.05 for contact periods of 30, 48, and 60 hr. In this study, S:L batch tests were performed on two selected soils: Umatilla and SE Fort Site 10, using varying concentrations of EDTA and HCl.

By selecting these varying soil types and extracting agents, the tests yielded a general S:L ratio that could be used on all types of soils to be investigated in the subsequent studies. The results also determined a time for the chemical reaction between the reagent and soil to reach steady state that could be used in future tests. All statistical analyses used in this particular batch test are provided in Appendix B. For sets of data to be considered significantly different, a 95-percent confidence criterion was established.

Results of the two S:L tests were combined to draw a comparison between all five S:L ratios being evaluated. Figures 8 and 9 show two of the results generated in these S:L tests: the Umatilla soil washed with EDTA and HCl for 30 hr. Both figures show the quantity of Pb removed per gram of soil versus the extracting agent concentrations using S:L ratios of 0.5, 0.2, 0.05, 0.01, and 0.005. The visual observations in Figure 8 showed little change in the amount of Pb washed from the soil between S:L ratios using an EDTA concentration of 0.01 M. On the other hand, when an EDTA concentration of 0.1 M was used, a general trend of increase in the

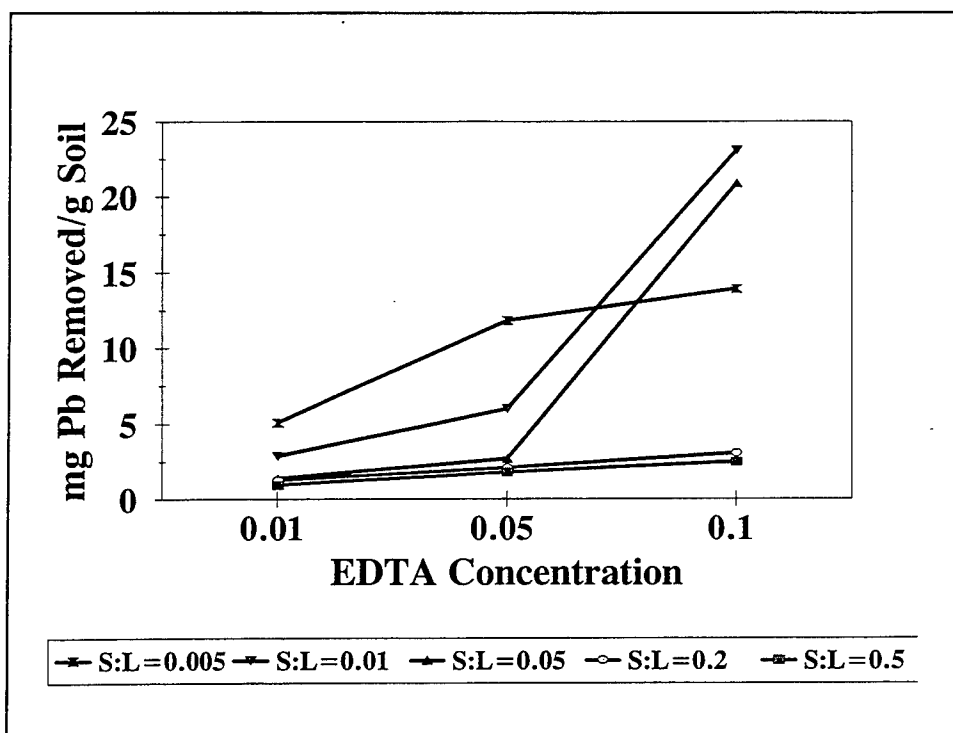


Figure 8. Solid-to-liquid ratio comparison using Umatilla soil and EDTA contacted for 30 hr

removal of Pb was seen as the S:L ratio decreased from a value of 0.5 to 0.01. To accurately determine the significance of the observed differences, an analysis of variance was performed on the data shown in Figure 8. In contrast to the observed differences found using an EDTA concentration of 0.1 M, the statistical analysis concluded that Pb removal was not significantly affected by a change in the S:L ratios as shown in Table 19.

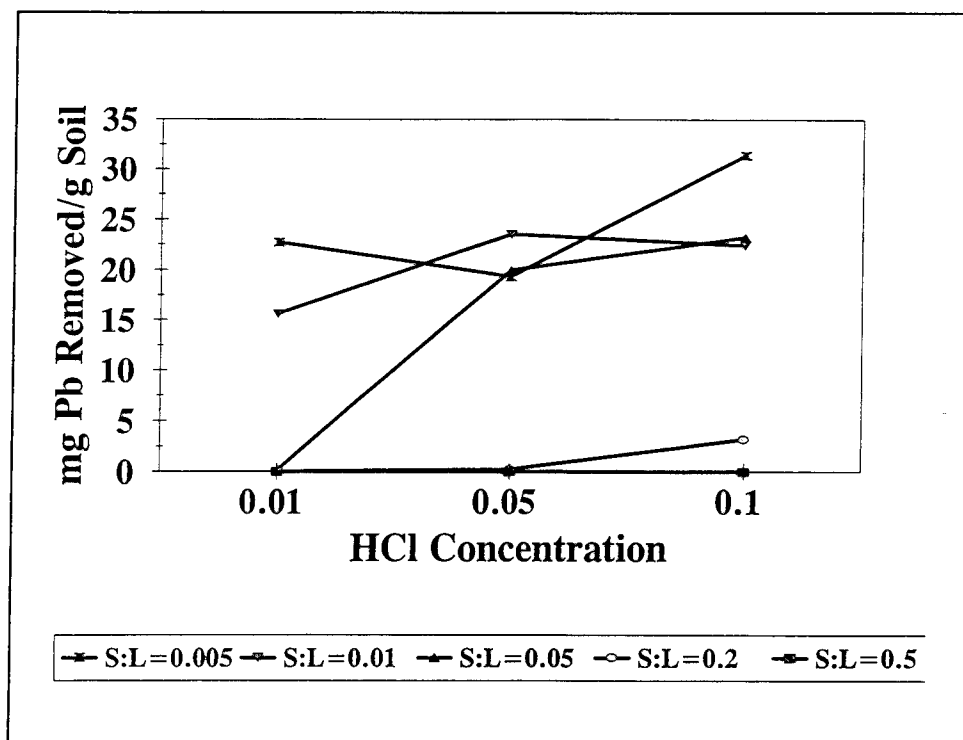


Figure 9. Solid-to-liquid ratio comparison using Umatilla soil and HCl contacted for 30 hr

Figure 9 shows the Pb removal efficiency from the Umatilla soil washed with HCl using a variety of S:L ratios ranging from 0.5 to 0.005. A difference in Pb removal was seen between the three smaller S:L ratios of 0.005, 0.01, and 0.05 versus the two larger S:L ratios of 0.2 and 0.5. The statistical analysis confirmed the observations and indicated a significant difference between the three smaller S:L ratios and the S:L ratios of 0.2 and 0.5 as shown in Table 20.

Overall, the observed results indicated that the three smaller S:L ratios were much more efficient for Pb extraction than the two larger ones. However, the analysis of variance of the data did not totally support the observed conclusions. Due to the trends observed and by maximizing extraction efficiency and S:L ratio, an S:L ratio of 0.05 appeared to be optimal. This selection process maximized the volume of soil treated per unit volume of extracting fluid.

The second objective of the S:L tests was to determine an appropriate reaction time for the soil and extracting agent to reach chemical steady state. By ensuring adequate contact time to optimize metal removal, an accurate comparison could be made between extracting agents regarding their ability to extract metals from soils. Using the optimal S:L ratio of 0.05, comparisons were made between contact periods of 24, 30, 48, and 60 hr. Some representative results are shown in Figures 10 and 11.

Table 19
Statistical Analysis Output for S:L Ratio Test Umatilla-EDTA-30 Hr

Analysis of Variance Procedure Class Level Information					
Class		Levels		Values	
SL Ratio		5		0.005, 0.01, 0.05, 0.2, 0.5	
Conc		3		0.01, 0.05, 0.1	
Number of observations in data set = 15					
Dependent variable: Pb					
Source	DF	ANOVA SS	Mean Square	F Value	Pr > F
SL Ratio	4	228.7474	57.1868	2.01	0.1862
Conc	2	291.6467	145.8233	5.12	0.0370
Waller-Duncan K-ratio T test for variable: Pb					
Note: This test minimizes the Bayes risk under additive loss and certain other assumptions.					
K ratio = 100 df = 8 MSE = 28.4746 F = 2.008345					
Critical Value of T = 2.67298					
Minimum Significant Difference = 11.646					
Means with the same letter are not significantly different.					
Waller Grouping	Mean		N	SL Ratio	
A	10.667		3	0.01	
A	10.267		3	0.005	
A	8.333		3	0.05	
A	2.148		3	0.2	
A	1.758		3	0.5	
Duncan's Multiple Range Test for Variable: Pb					
Note: This test controls the Type I comparisonwise error rate, not the experimentwise error rate.					
Alpha = 0.05 df = 8 MSE = 28.4746					
Number of Means 2 3 4 5					
Critical Range 10.05 10.47 10.71 10.85					
Means with the same letter are not significantly different.					
Waller Grouping	Mean		N	SL Ratio	
A	10.667		3	0.01	
A	10.267		3	0.005	
A	8.333		3	0.05	
A	2.148		3	0.2	
A	1.758		3	0.5	

Table 20
Statistical Analysis Output for S:L Ratio Test Umatilla-HCI-30 Hr

Analysis of Variance Procedure Class Level Information					
Class		Levels		Values	
SL Ratio		5		0.005, 0.01, 0.05, 0.2, 0.5	
Conc		3		0.01, 0.05, 0.1	
Number of observations in data set = 15					
Dependent variable: Pb					
Source	DF	ANOVA SS	Mean Square	F Value	Pr > F
SL Ratio	4	1486.2165	371.5541	11.58	0.0021
Conc	2	176.4816	88.2408	2.75	0.1232
Waller-Duncan K-ratio T test for variable: Pb					
Note: This test minimizes the Bayes risk under additive loss and certain other assumptions.					
K ratio = 100 df = 8 MSE = 32.0738 F = 11.58434					
Critical Value of T = 2.28590					
Minimum Significant Difference = 10.57					
Means with the same letter are not significantly different.					
Waller Grouping		Mean	N	SL Ratio	
A		24.467	3	0.005	
A		20.500	3	0.01	
A		14.400	3	0.05	
	B	1.130	3	0.2	
	B	0.005	3	0.5	
Duncan's Multiple Range Test for Variable: Pb					
Note: This test controls the Type I comparisonwise error rate, not the experimentwise error rate.					
Alpha = 0.05 df = 8 MSE = 32.0738					
Number of Means 2 3 4 5					
Critical Range 10.66 11.11 11.36 11.51					
Means with the same letter are not significantly different.					
Duncan Grouping		Mean	N	SL Ratio	
A		24.467	3	0.005	
A		20.500	3	0.01	
A		14.400	3	0.05	
	B	1.130	3	0.2	
	B	0.005	3	0.5	

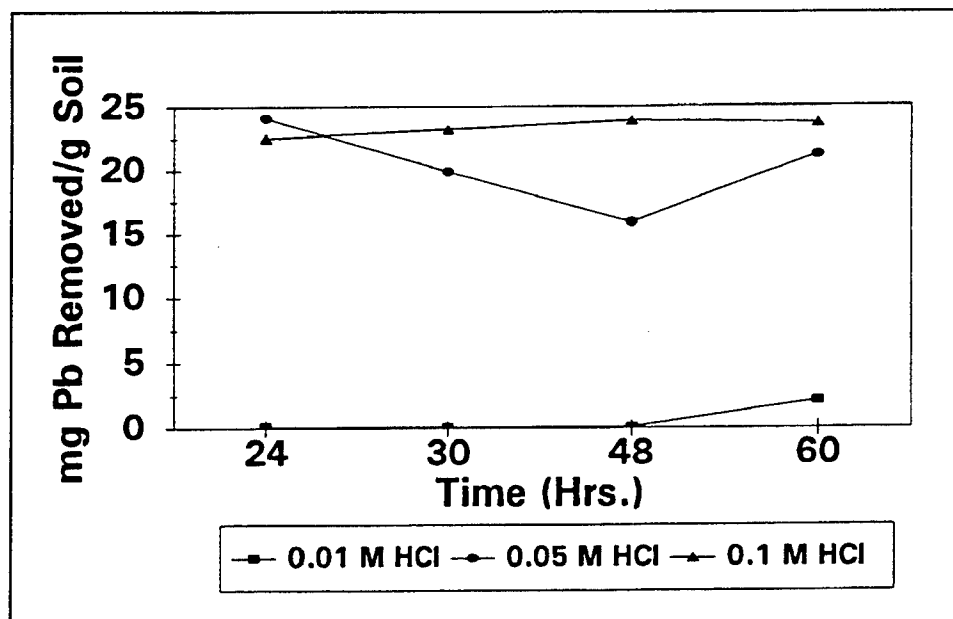


Figure 10. Comparison of reaction times to reach steady state using Umatilla soil, HCl, and an S:L ratio of 0.05

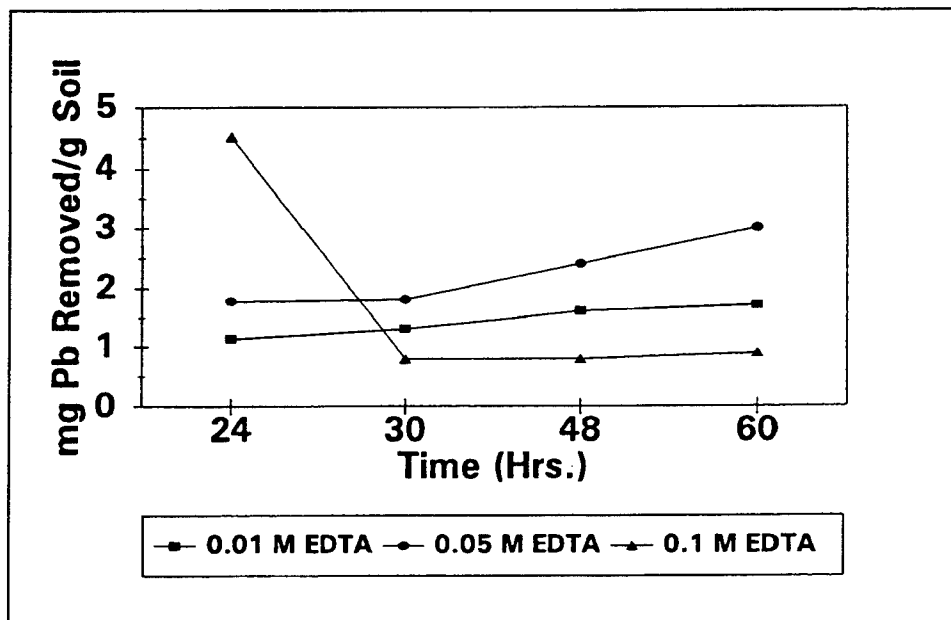


Figure 11. Comparison of reaction times to reach steady state using SE Fort Site 10 soil, EDTA, and an S:L ratio of 0.05

Figure 10 compares the effectiveness of Pb extraction from the Umatilla soil using HCl at 24, 30, 48, and 60 hr. The removal efficiency changed very little over the four time periods. This observation was supported by the statistical analysis of variance, which suggested that Pb removal was not affected by an increase in

reaction time (Table 21). Figure 11 compares Pb extraction from the SE Fort Site 10 soil using EDTA at the various contact time intervals. Again, Pb extraction was generally not increased by increasing the contact time between soil and extracting agent. In support of the observations, the statistical analysis of variance showed no significant difference in Pb removal versus an increase in contact time (Table 22).

Table 21					
Statistical Analysis Output for S:L Ratio Test Umatilla-HCl-					
S:L = 0.05					
Analysis of Variance Procedure Class Level Information					
Class	Levels		Values		
SL Ratio Times	4		24, 30, 48, 60		
Conc	3		0.01, 0.05, 0.1		
Number of observations in data set = 12					
Dependent variable: Pb					
Source	DF	ANOVA SS	Mean Square	F Value	Pr > F
SL Ratio Times	3	11.4073	3.8024	0.82	0.5281
Conc	2	1218.2964	609.1482	131.52	0.0001
Waller-Duncan K-ratio T test for variable: Pb					
Note: This test minimizes the Bayes risk under additive loss and certain other assumptions.					
Error: Failure in Bayes T computation. F value of 0.82 too small.					

Table 22					
Statistical Analysis Output for S:L Ratio Test SE Fort Site 10-EDTA-					
S:L = 0.05					
Analysis of Variance Procedure Class Level Information					
Class		Levels		Values	
SL Ratio Times		4		24, 30, 48, 60	
Conc		3		0.01, 0.05, 0.1	
Number of observations in data set = 12					
Dependent variable: Pb					
Source	DF	ANOVA SS	Mean Square	F Value	Pr > F
SL Ratio Times	3	2.2369	0.7456	0.49	0.7035
Conc	2	1.3337	0.6668	0.44	0.6657
Waller-Duncan K-ratio T test for variable: Pb					
Note: This test minimizes the Bayes risk under additive loss and certain other assumptions.					
Error: Failure in Bayes T computation. F value of 0.49 is too small.					

Based on these results, 24 hr was a suitable time for the soil and extracting agent to reach chemical steady state. To ensure that steady state was reached in the experiments conducted as part of this study, samples were contacted 6 extra hr for a total of 30 hr contact time.

Extractant effectiveness test

As evidenced in previous studies, the range of metal removal efficiencies varies greatly with the type of extracting agent, extracting agent concentration, and the metal targeted for removal. The removal efficiency of Pb from soils ranged from 2 percent using 0.1 M NTA (Peters and Shem 1991) to 99 percent using fluorosilicic acid (Royer, Selvakumar, and Gaire 1992). The removal efficiency of Cd from soils ranged from 39 percent using 0.1 M HNO₃ (Mortazavi, Volchek, and Whittaker 1992) to 67.9 percent using 1.0 M HCl (Neuhauser and Hartenstein 1980). For Cr, the removal efficiencies ranged from 5 percent using 0.1 M HCl (Tuin and Tels 1990b) to 55.6 percent using 1.0 M HCl (Neuhauser and Hartenstein 1980). The major objective of the extractant effectiveness test was to evaluate the selected extracting agents on their ability to remove these metals from contaminated soils. To meet this objective, all of the selected soils and extracting agents were incorporated into the experiment. Further, each of the extracting agents was tested at three concentrations including 0.01 M, 0.05 M, and 0.1 M. This test also used parameters that were determined in the solid-to-liquid ratio test including an S:L ratio of 0.05 and a reaction time of 30 hr.

Pb extraction results

Six of the selected soils including Umatilla, Fort Ord, SE Fort Sites 5-8, SE Fort Site 10, SE Fort Site 12, and WES spiked soil contained large concentrations of Pb and were contacted with three concentrations of each of the extracting agents. The results of these extractions are presented in Figures 12-17.

Figure 12 illustrates Pb removal from the sandy Umatilla soil. For this soil, 99 percent of Pb was removed using 0.05 M and 0.1 M concentrations of HNO₃, HCl, and fluorosilicic acid. Also, 0.1 M citric acid, 0.01 M NTA, and 0.1 M NTA were able to extract 99 percent of Pb from the soil. The poor removal efficiency of 0.05 M NTA can most likely be attributed to the heterogeneity of the Umatilla soil samples used in the three NTA shaker tests. EDTA and NaOH were not as successful as the other extracting agents at removing Pb from the Umatilla soil. EDTA removed a maximum of 36 percent Pb from the soil at a concentration of 0.1 M, while NaOH extracted a maximum of 34 percent Pb at a concentration of 0.1 M.

Figure 13 presents Pb removal from the Fort Ord soil. The three strong acids, HNO₃, HCl, and fluorosilicic acid, performed much better than the chelating agents. Ninety-nine percent of Pb was removed using a 0.05 M concentration of HNO₃, while 90 percent Pb extraction was achieved by 0.05 M fluorosilicic acid. Of the four chelating agents, only 0.05 M NTA was able to remove more than 60 percent of Pb from the soil.

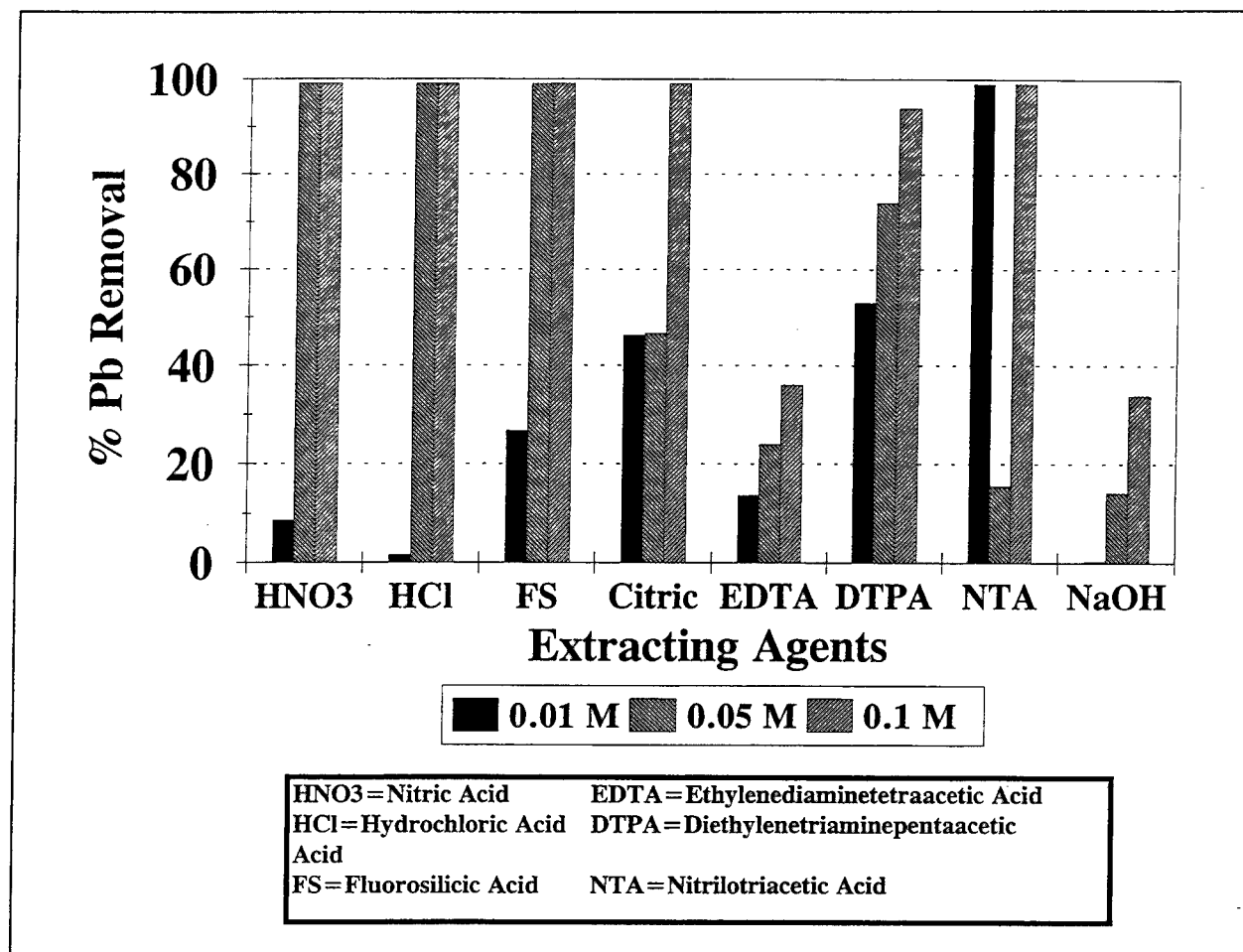


Figure 12. Pb removal efficiency versus extracting agents for Umatilla soil

Figure 14 represents Pb removal from the SE Fort Sites 5-8 clay/sand soil mix. All three strong acids achieved 99-percent Pb removal at the two higher concentrations. The most effective chelating agents were DTPA and NTA, both of which removed 99 percent of Pb from the soil at all three concentrations. As in the SE Fort Site 12 extraction test, little difference in metal removal was seen as the reagent concentration increased from 0.05 M to 0.1 M. Maximum Pb removal efficiencies for citric acid, EDTA, and NaOH were 69, 86, and 89 percent, respectively, at a concentration of 0.1 M.

Figure 15 presents Pb removal from the SE Fort Site 10 clayey soil. Concentrations of 0.05 M HNO₃ and 0.01 M HCl resulted in 99-percent removal of Pb from the soil. Both of these acids were much more effective at Pb removal than fluorosilicic acid, which achieved a maximum of 38-percent contaminant removal at a concentration of 0.05 M. Ninety-nine percent of the Pb in the soil was extracted using 0.1 M citric acid or 0.1 M DTPA. In the case of both of these reagents, Pb extraction increased dramatically with an increase in solution concentration from 0.05 M to 0.1 M. NTA and NaOH were relatively ineffective at removing Pb from the SE Fort Site 10 soil.

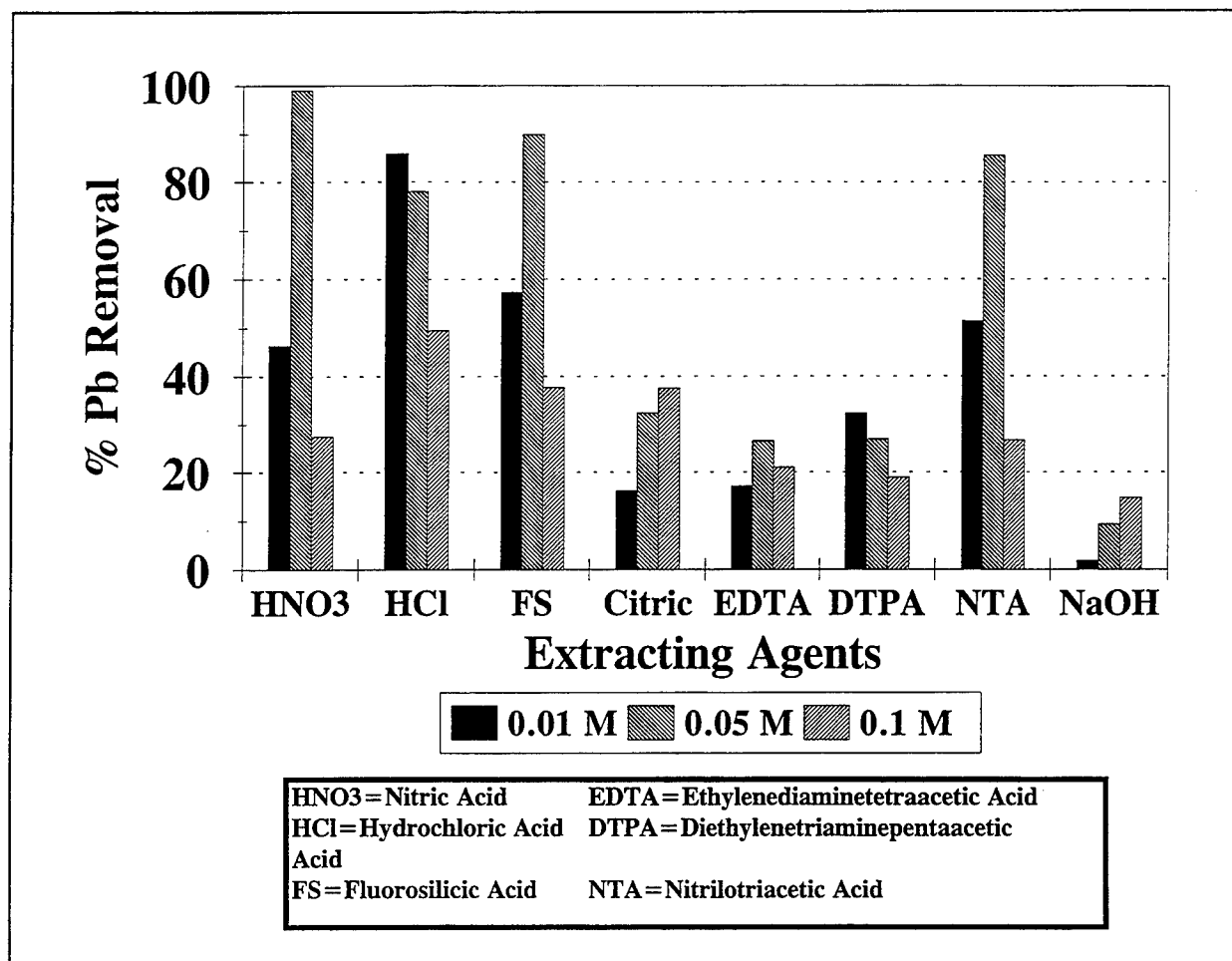


Figure 13. Pb removal efficiency versus extracting agents for Fort Ord soil

Figure 16 presents Pb removal from the SE Fort Site 12 soil. As expected, all of the reagents were much more effective at removing Pb from this sandy soil than from the clayey SE Fort Site 10 soil. Ninety-nine percent Pb removal was achieved at all concentrations of HNO₃ and NTA, at 0.05 M and 0.1 M concentrations of HCl and fluorosilicic acid, and at a 0.1 M concentration of citric acid. The quantity of metal removal was not significantly affected by an increase in reagent concentration from 0.05 M to 0.1 M. Maximum Pb removal using EDTA was 83 percent at a concentration of 0.1 M, while optimal Pb removal using DTPA was 84 percent at a concentration of 0.05 M. Optimal Pb removal using NaOH was 52 percent at a concentration of 0.1 M.

Figure 17 illustrates the rate of Pb removal from the WES spiked soil. Whereas the strong acids generally outperformed the chelating agents in the removal of Pb from the soils in the environment, the chelating agents extracted more Pb than the strong acids from the spiked soil. EDTA and NTA each extracted nearly 99 percent of Pb from the soil using concentrations of 0.05 M or 0.1 M. DTPA extracted 99 percent of Pb from the soil, regardless of the concentration used. Of the three

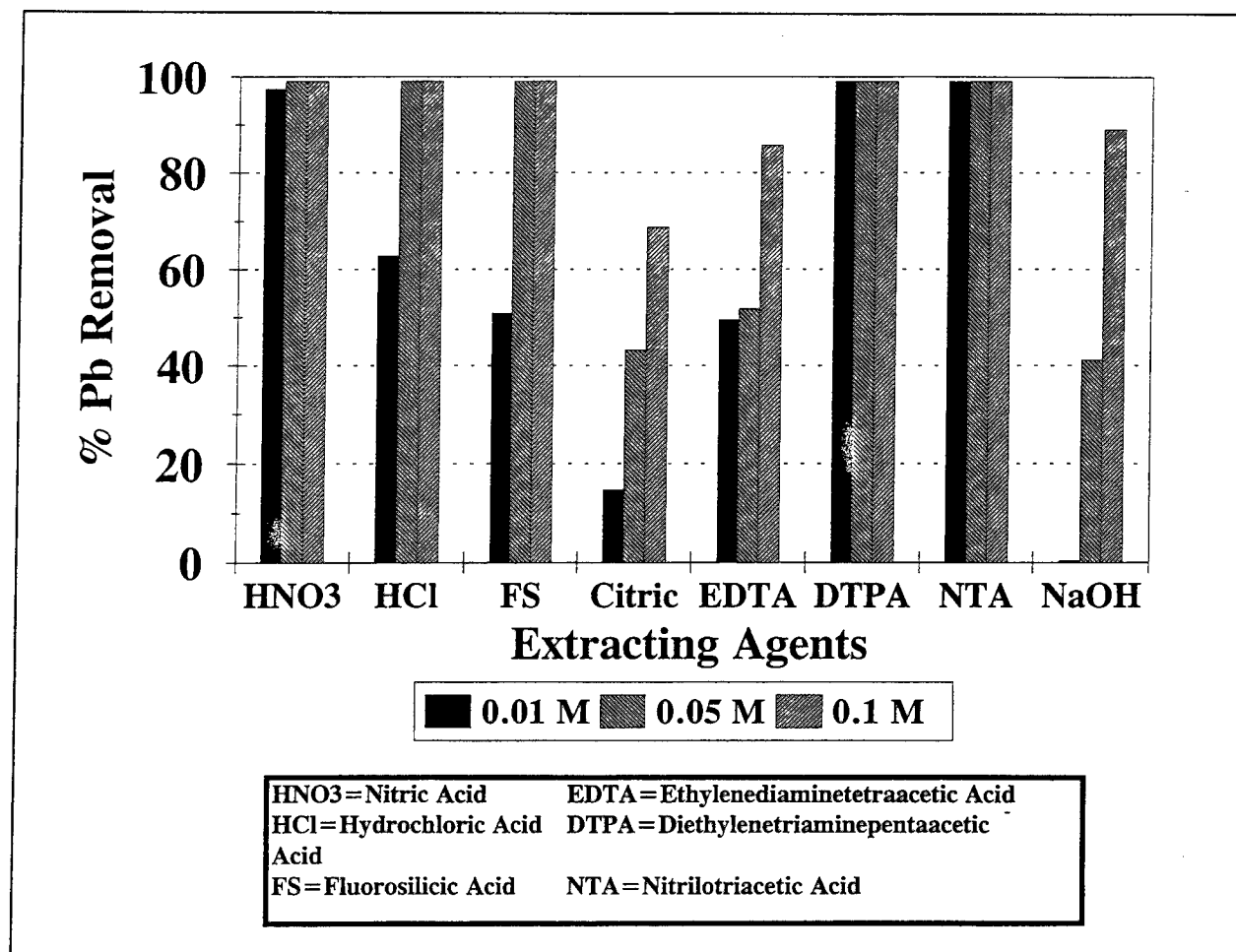


Figure 14. Pb removal efficiency versus extracting agents for SE Fort Sites 5-8 soil

strong acids, only fluorosilicic acid was able to extract nearly all of the Pb from the soil.

Deriving a conclusion concerning the best extracting agents and concentration from the preceding visual observations was extremely difficult. Therefore, a statistical analysis of variance was performed on the data to determine which extracting agents and which concentrations were most effective at Pb removal. The entire statistical analysis is presented in Appendix C. A portion of the analysis is presented in Table 23. Comparing the mean Pb removal efficiencies of each of the extracting agents, fluorosilicic acid (67.2 percent) and HCl (67.1 percent) were the most effective extracting agents followed closely by HNO₃ (67.0 percent), NTA (66.9 percent), and DTPA (64.5 percent). Citric acid (54.8 percent) and EDTA (46.5 percent) were the next most efficient Pb extracting agents, while NaOH (16.1 percent) was the least effective extracting agent. As expected, the statistical analysis of the variance (at the 95-percent confidence level) also indicated that there was no significant difference between the removal efficiencies of fluorosilicic acid, HCl, HNO₃, NTA, DTPA, and citric acid. Since NTA is a suspected carcinogen and

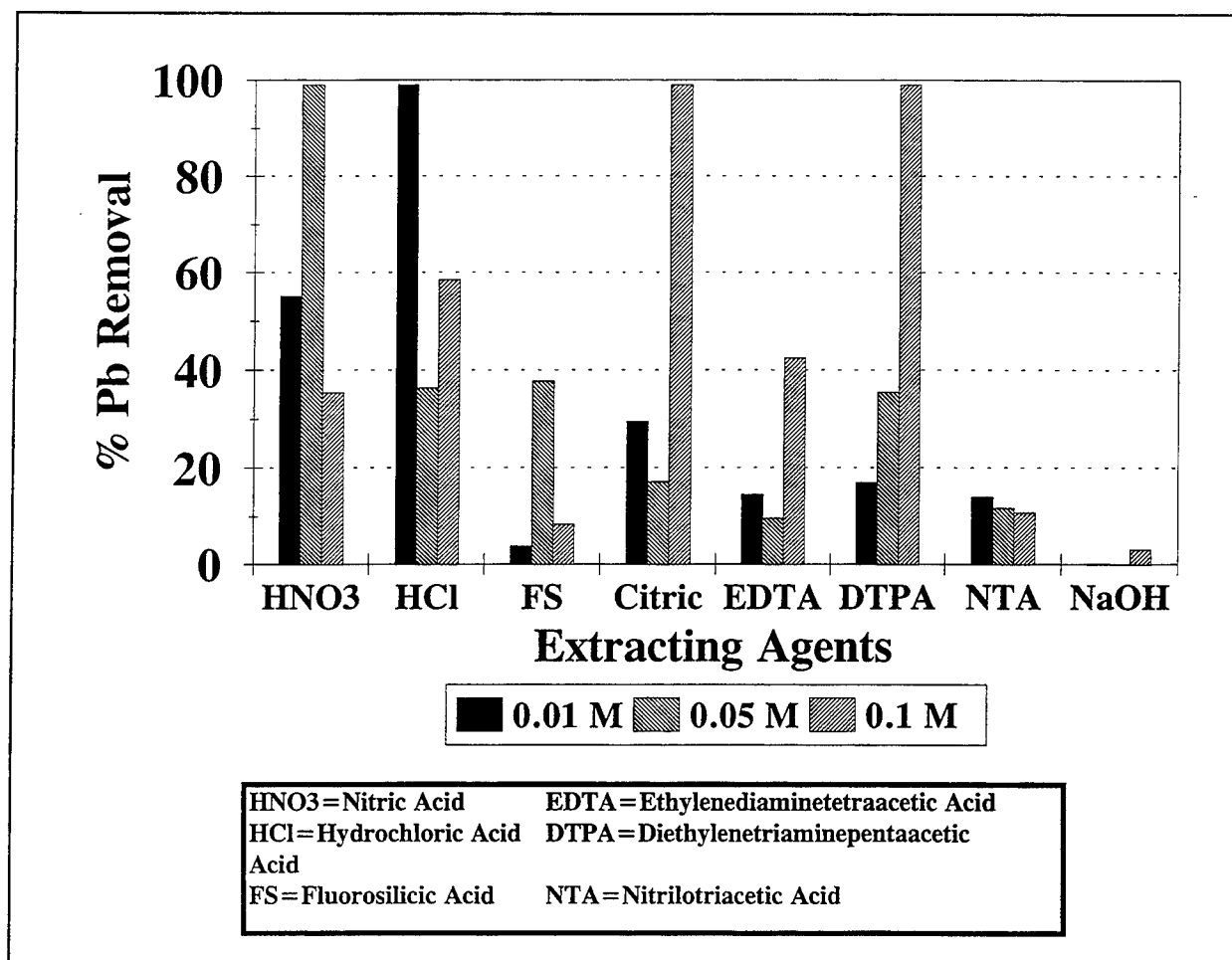


Figure 15. Pb removal efficiency versus extracting agents for SE Fort Site 10 soil

fluorosilicic acid is an extremely aggressive reagent and can destroy the matrices of soils (both undesirable properties of extractants), neither of these two extracting agents were suitable for use in the pilot-scale countercurrent metal extraction system. Therefore, HNO₃, HCl, DTPA, and citric acid were selected as the best extracting agents for the removal of Pb from these soils.

The analysis of variance also compared the three extracting agent concentrations to analyze the significant differences between them. These results indicated that concentration of 0.05 M and 0.1 M was not significantly different; however, both of these concentrations were significantly better for Pb extraction than 0.01 M. To minimize the concentration of the extracting agent used in testing without reducing the concentration of Pb removed from the soils, a concentration of 0.05 M was selected as the optimal concentration for the removal of Pb from the selected soils.

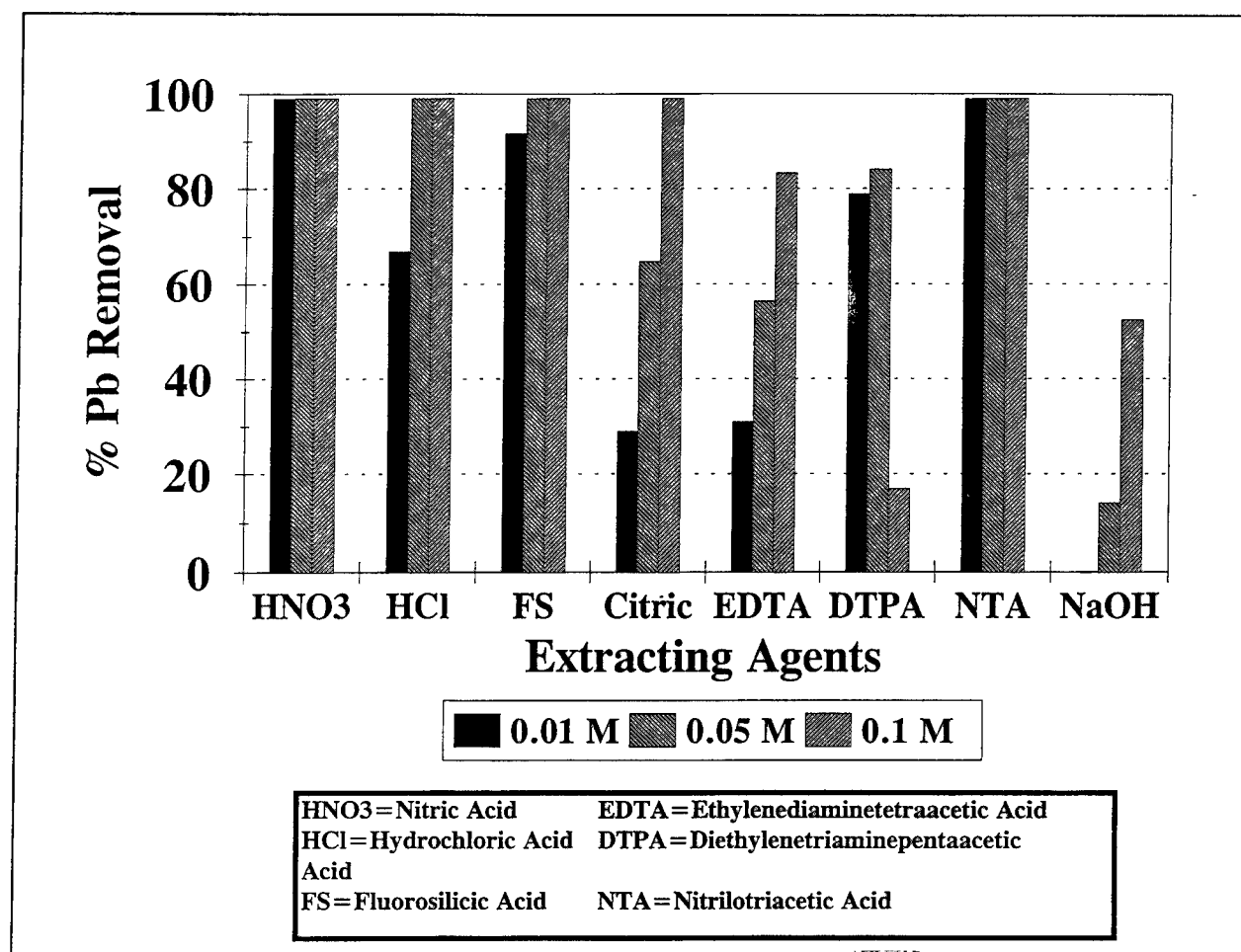


Figure 16. Pb removal efficiency versus extracting agents for SE Fort Site 12 soil

Cd extraction results

Two of the eight selected soils, including the LAAP Site 2 and WES spiked soils, contained large concentrations of Cd and were contacted with three concentrations of each of the extracting agents to determine an optimal extracting agent and concentration for the removal of Cd. The results of these extractions are presented in Figures 18 and 19.

Figure 18 presents Cd removal from the LAAP Site 2 clay/silt soil. A high degree of Cd extraction was achieved by all of the strong acids and some of the chelating agents. Concentrations of 0.05 M and 0.1 M of HNO₃, HCl, fluorosilicic acid, citric acid, and NTA extracted 99 percent of Cd from this soil. A concentration of 0.1 M EDTA removed 97 percent of Cd from the soil, while 85 percent of Cd was extracted from the LAAP Site 2 soil using 0.01 M DTPA. NaOH was ineffective at Cd removal.

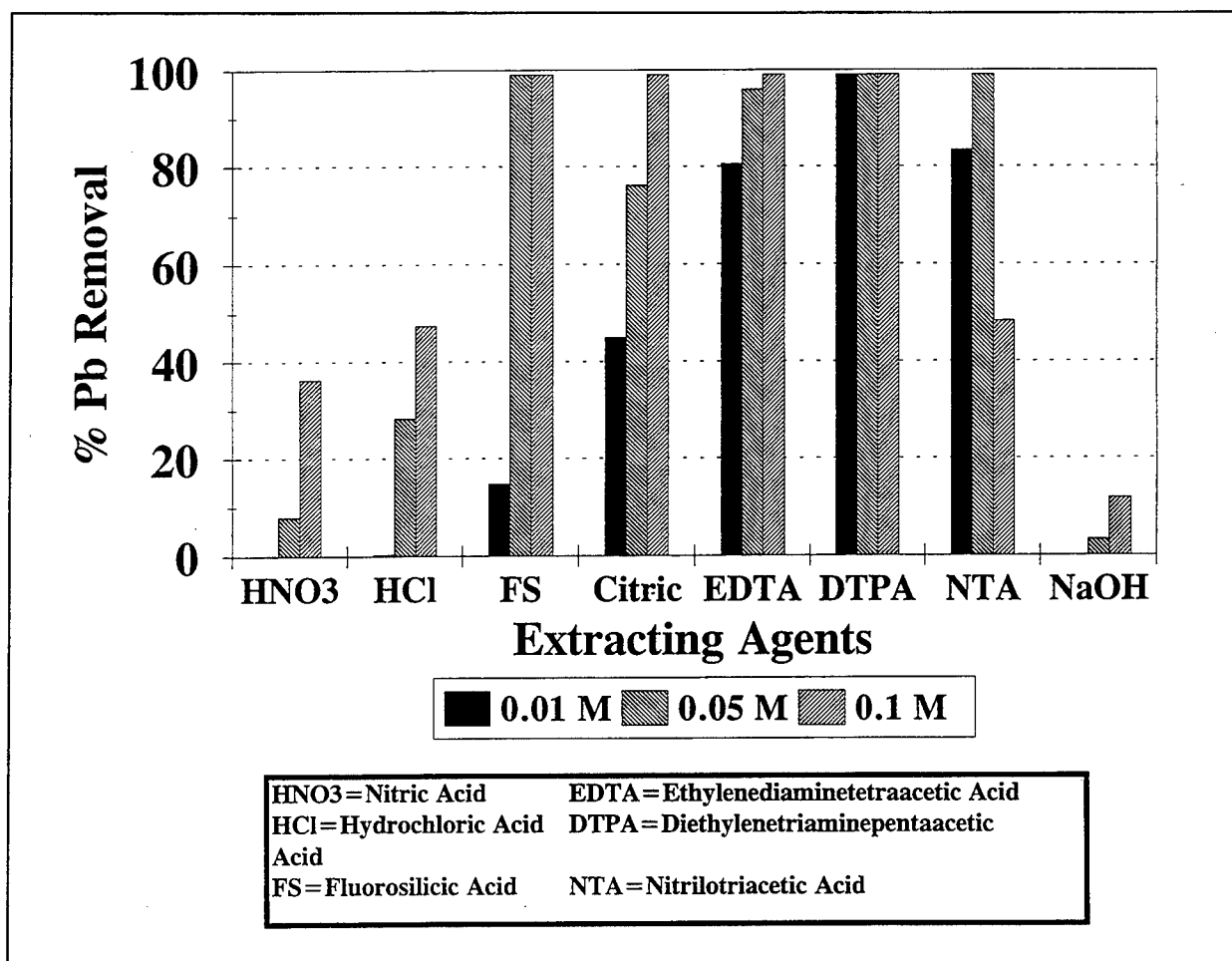


Figure 17. Pb removal efficiency versus extracting agents for WES spiked soil

Figure 19 represents Cd removal from the WES spiked soil. All of the extracting agents except NaOH achieved 99-percent Cd removal from the soil using at least one of the concentrations that were evaluated. Fluorosilicic acid and DTPA extracted 99 percent of Cd from the WES spiked soil at all concentrations, while HNO₃, EDTA, and NTA each removed at least 90 percent of Cd for all concentrations. The two higher concentrations of HCl and citric acid removed 99 percent of Cd from the WES spiked soil.

These visual observations indicate very little difference in the extracting agents with the exception of NaOH. Further, very little change in the removal of Cd was observed over the entire range of extracting agent concentrations being evaluated. A statistical analysis of variance was also performed on this data to determine any significant differences (at the 95-percent confidence) between extracting agents and any differences between concentrations. The analysis of variance is provided in Appendix C. A portion of the analysis is presented in Table 24. In the Waller-Duncan grouping of the extracting agents, the analysis indicated that NaOH is the only extract producing significantly different results. The analysis further indicated that no significant differences were found between the reagent concentrations

Table 23
Statistical Analysis Output for Extractant Effectiveness Test, Pb-Contaminated Soils

Analysis of Variance Procedure Class Level Information					
Class		Levels		Values	
Soil		6		Uma, SEF10, SEF12, SEF5-8, Ord, WES	
Ext		8		HNO ₃ , HCl, FS, Citric, EDTA, DTPA, NTA, NaOH	
Conc		3		0.01, 0.05, 0.1	
Number of observations in data set = 144					
Dependent variable: Pb					
Source	DF	ANOVA SS	Mean Square	F Value	Pr > F
Soil	5	30223.7373	6044.7475	7.28	0.0001
Ext	7	40455.5544	5779.3649	6.96	0.0001
Conc	2	16891.6654	8445.8327	10.17	0.0001
Waller-Duncan K-ratio T test for variable: Pb					
Note: This test minimizes the Bayes risk under additive loss and certain other assumptions.					
K ratio = 100 df = 129 MSE = 830.6899 F = 6.957308					
Critical Value of T = 1.89042					
Minimum Significant Difference = 18.162					
Means with the same letter are not significantly different.					
Waller Grouping			Mean	N	Ext
A			67.256	18	FS
A			67.133	18	HCl
A			66.972	18	HNO ₃
A			66.900	18	DTPA
A	B		64.539	18	NTA
A	B		54.761	18	Citric
	B		46.511	18	EDTA
		C	16.078	18	NaOH
K-ratio = 100 df = 129 MSE = 830.6899 F = 10.16725					
Critical Value of T = 1.84290					
Minimum Significant Difference = 10.842					
(Continued)					

Table 23 (Concluded)								
Means with the same letter are not significantly different.								
Waller Grouping		Mean	N	Conc				
A		66.127	48	0.1 M				
A		61.492	48	0.05 M				
	B	41.188	48	0.01 M				
Duncan's Multiple Range Test for Variable: Pb								
Note: This test controls the Type I comparisonwise error rate, not the experimentwise error rate.								
Alpha = 0.05 df = 129 MSE = 830.6899								
Number of Means		2	3	4	5	6	7	8
Critical Range		19.01	20.01	20.67	21.16	21.56	21.86	22.10
Means with the same letter are not significantly different.								
Duncan Grouping		Mean	N	Ext				
A		67.256	18	FS				
A		67.133	18	HCl				
A		66.972	18	HNO ₃				
A		66.900	18	DTPA				
A		64.539	18	NTA				
A		54.761	18	Citric				
A		46.511	18	EDTA				
	B	16.078	18	NaOH				
Alpha = 0.05 df = 129 MSE = 830.6899								
Number of Means		2	3					
Critical Range		11.64	12.25					
Means with the same letter are not significantly different.								
Duncan Grouping		Mean	N	Conc				
A		66.127	48	0.1 M				
A		61.492	48	0.05 M				
	B	41.188	48	0.01 M				

0.01 M and 0.05 M or the concentrations of 0.05 M and 0.01 M; however, the analysis showed that a concentration of 0.1 M was significantly more effective in Cd removal than a concentration of 0.01M.

Since there were no significant differences between any of the extracting agents, HNO₃, citric acid, HCl, and EDTA were selected as the most effective extracting agents for the removal of Cd from the soils. Since the percentage of Cd removal was not affected by an increase in extracting agent concentration from 0.05 M to 0.1 M, the optimal concentration for Cd removal was 0.05 M.

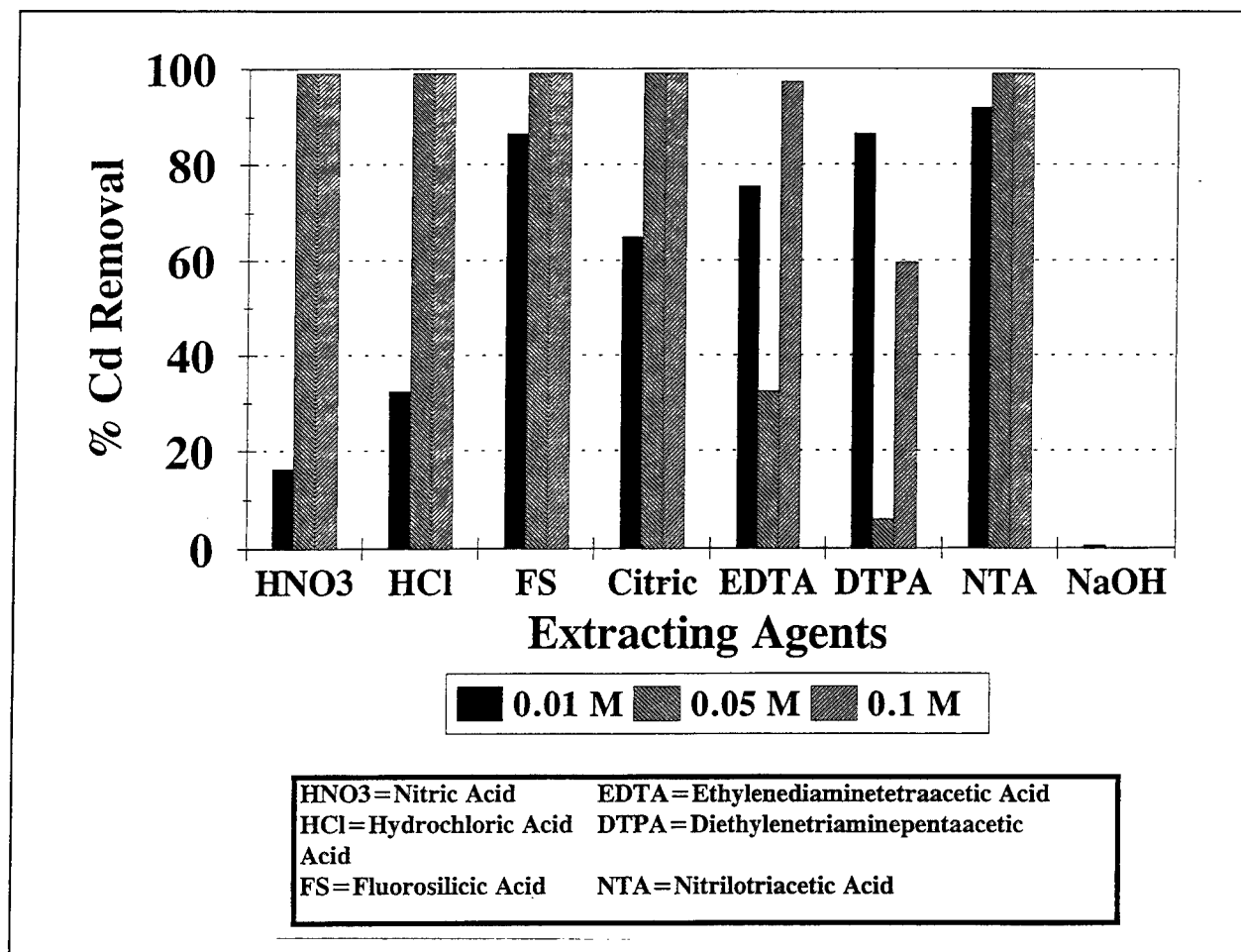


Figure 18. Cd removal efficiency versus extracting agents for LAAP Site 2 soil

Cr extraction results

Three of the eight selected soils, including LAAP Site 1, LAAP Site 2, and WES spiked soil, contained appreciable concentrations of Cr, and all of the extracting agents were evaluated on their ability to remove Cr from these soils. The results of these extractions are presented in Figures 20-22.

Figure 20 shows Cr removal from the LAAP Site 1 clay/silt soil. The most effective reagent for Cr removal was 0.1 M fluorosilicic acid, which extracted 51 percent of Cr from the soil. Concentrations of 0.1 M HNO₃ and 0.1 M HCl leached 41 and 33 percent of Cr from the soil, respectively. Both NTA and citric acid removed approximately 30 percent of Cr from the LAAP Site 1 soil for all concentrations. NaOH removed 18 percent of Cr at a concentration of 0.1 M.

Figure 21 presents Cr extraction from the LAAP Site 2 clay/silt soil. Concentrations of 0.1 M fluorosilicic acid and 0.1 M citric acid removed 99 percent and 74 percent of Cr from the soil, respectively. HNO₃ and HCl extracted greater than 50 percent of Cr from the soil at a concentration of 0.1 M. The other extracting

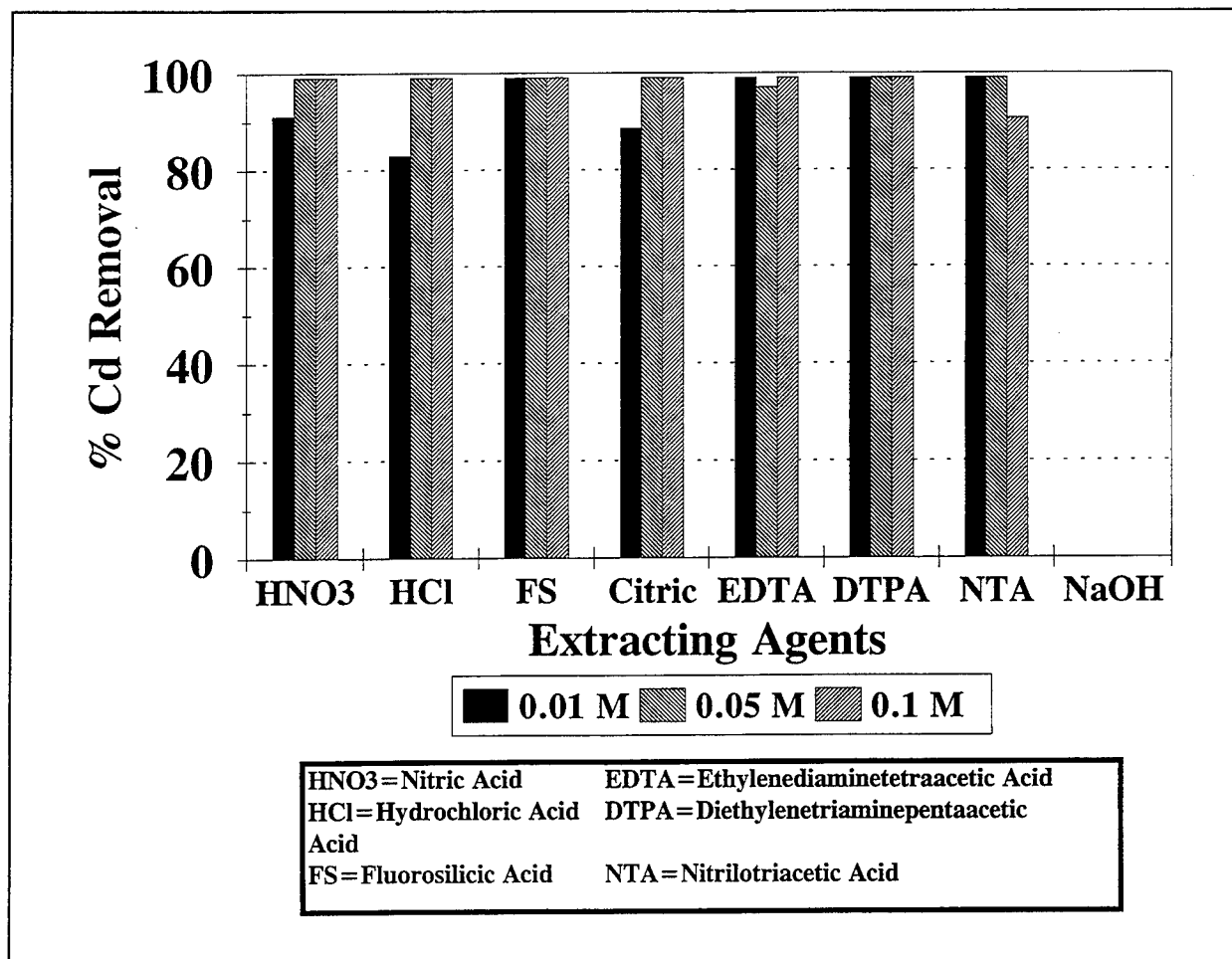


Figure 19. Cd removal efficiency versus extracting agents for WES spiked soil

agents were not able to remove appreciable quantities of Cr from the LAAP Site 2 soil.

Figure 22 shows Cr removal from the WES spiked soil. As with the Cr extraction test on the LAAP Site 2 soil, fluorosilicic acid and citric acid were the two most effective extracting agents for the removal of Cr from the WES spiked soil. Fluorosilicic acid extracted 99 percent of Cr from the soil at concentrations of 0.05 M and 0.1 M. Citric acid removed 63 percent of Cr from the soil using a concentration of 0.1 M. The remaining reagents were ineffective.

Based on inspection and on average removal efficiencies for all soils examined, the best extracting agents for the removal of Cr from soils were fluorosilicic acid (53.7 percent) and citric acid (38.3 percent). These reagents were followed by HNO₃ (19.3 percent), HCl (16.6 percent), NTA (13.4 percent), NaOH (5.8 percent), EDTA (1.7 percent), and DTPA (1.2 percent). A statistical analysis of variance was carried out on the Cr extraction results and is provided in Appendix C. A portion of the data is presented in Table 25. The observations based on the graphical data are supported by statistical data that also showed that fluorosilicic acid and citric acid

Table 24
Statistical Analysis Output for Extractant Effectiveness Test, Cd-
Contaminated Soils

Analysis of Variance Procedure Class Level Information					
Class		Levels		Values	
Soil		2		LAAPS2, WES	
Ext		8		HNO ₃ , HCl, FS, Citric, EDTA, DTPA, NTA, NaOH	
Conc		3		0.01, 0.05, 0.1	
Number of observations in data set = 48					
Dependent variable: Cd					
Source	DF	ANOVA SS	Mean Square	F Value	Pr > F
Soil	1	2625.5208	2625.5208	6.09	0.0183
Ext	7	42447.0867	6063.8695	14.08	0.0001
Conc	2	2176.8054	1088.4027	2.53	0.0936
Waller-Duncan K-ratio T test for variable: Cd					
Note: This test minimizes the Bayes risk under additive loss and certain other assumptions.					
K ratio = 100 df = 37 MSE = 430.7742 F = 14.07668					
Critical Value of T = 1.87271					
Minimum Significant Difference = 22.441					
Means with the same letter are not significantly different.					
Waller Grouping		Mean	N	Ext	
A		96.92	6	FS	
A		96.42	6	NTA	
A		91.57	6	Citric	
A		85.22	6	HCl	
A		83.88	6	HNO ₃	
A		83.65	6	EDTA	
A		81.12	6	DTPA	
	B	0.10	6	NaOH	
K-ratio = 100 df = 37 MSE = 430.7742 F = 2.52662					
Critical Value of T = 2.22589					
Minimum Significant Difference = 16.334					
(Continued)					

Table 24 (Concluded)				
Means with the same letter are not significantly different.				
Waller Grouping		Mean	N	Conc
A		85.994	16	0.1 M
A	B	76.519	16	0.05 M
	B	69.563	16	0.01 M
Duncan's Multiple Range Test for Variable: Cd				
Note: This test controls the Type I comparisonwise error rate, not the experimentwise error rate.				
Alpha = 0.05 df = 37		MSE = 430.7742		
Number of Means		2	3	4
Critical Range		24.28	25.53	26.34
			26.92	27.37
				27.72
				28.01
Means with the same letter are not significantly different.				
Duncan Grouping		Mean	N	Ext
A		96.92	6	FS
A		96.42	6	NTA
A		91.57	6	Citric
A		85.22	6	HCl
A		83.88	6	HNO ₃
A		83.65	6	EDTA
A		81.12	6	DTPA
	B	0.10	6	NaOH
Alpha = 0.05 df = 37		MSE = 430.7742		
Number of Means		2	3	
Critical Range		14.87	15.63	
Means with the same letter are not significantly different.				
Duncan Grouping		Mean	N	Conc
A		85.994	16	0.1 M
A	B	76.517	16	0.05 M
	B	69.563	16	0.01 M

were the two most effective reagents for the removal of Cr. Of the remaining extracting agents, no statistically significant differences were found between HNO₃, HCl, NTA, and NaOH although EDTA and DTPA are significantly different. Since fluorosilicic acid is not suitable for use in the pilot-scale system, citric acid, HNO₃ and HCl were selected as the best extracting agents for use in the pilot studies. Analysis of the three concentrations revealed that concentrations of 0.05 M and 0.1 M were not significantly different from each other. However, the analysis did suggest a significant difference between the two higher concentrations and the

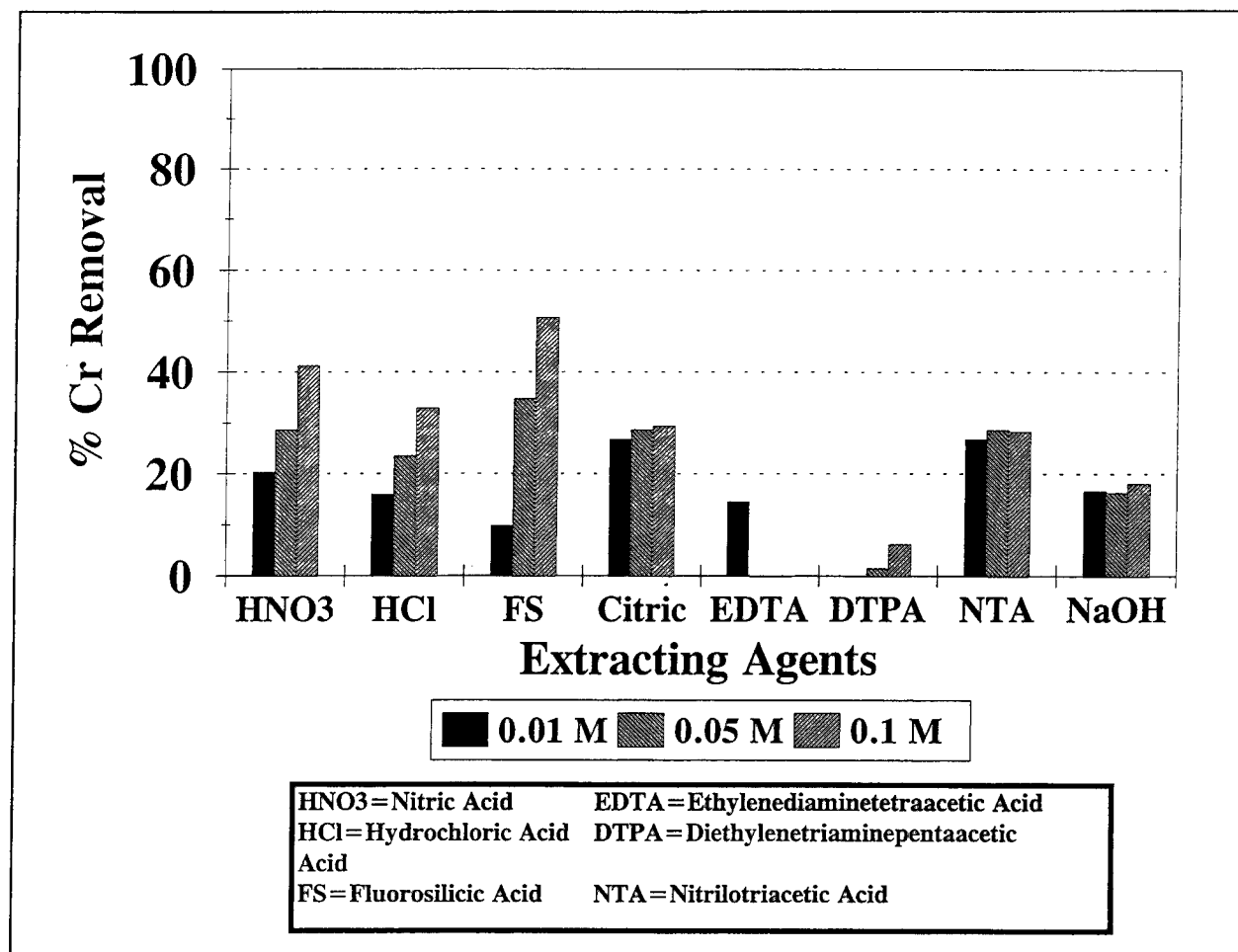


Figure 20. Cr removal efficiency versus extracting agents for LAAP Site 1 soil

0.01 M concentration. Both of the higher concentrations had a greater Cr removal efficiency than did 0.01 M. To minimize concentration without affecting Cr removal efficiency, an optimal concentration of 0.05 M was selected for use with all extracting agents and soils for the removal of Cr in the pilot studies.

Incorporating both observed and statistically analyzed results, a selection of the best extracting agents and the most effective concentration was performed for each metal in this study and is shown in Table 26. Excluding NTA and fluorosilicic acid from further consideration due to their toxicity, the most effective extracting agents for the removal of Pb were HCl, HNO₃, DTPA, and citric acid. For Cd, the most effective extracting agents were HNO₃, citric acid, HCl, and EDTA. Citric acid was the most effective extracting agent for the leaching of Cr from the selected soils. For all of the metals, the most efficient and effective extracting agent concentration was 0.05 M.

This batch study was designed to narrow the list of extracting agents, concentration of extracting agents, and soils that were considered for evaluation in further

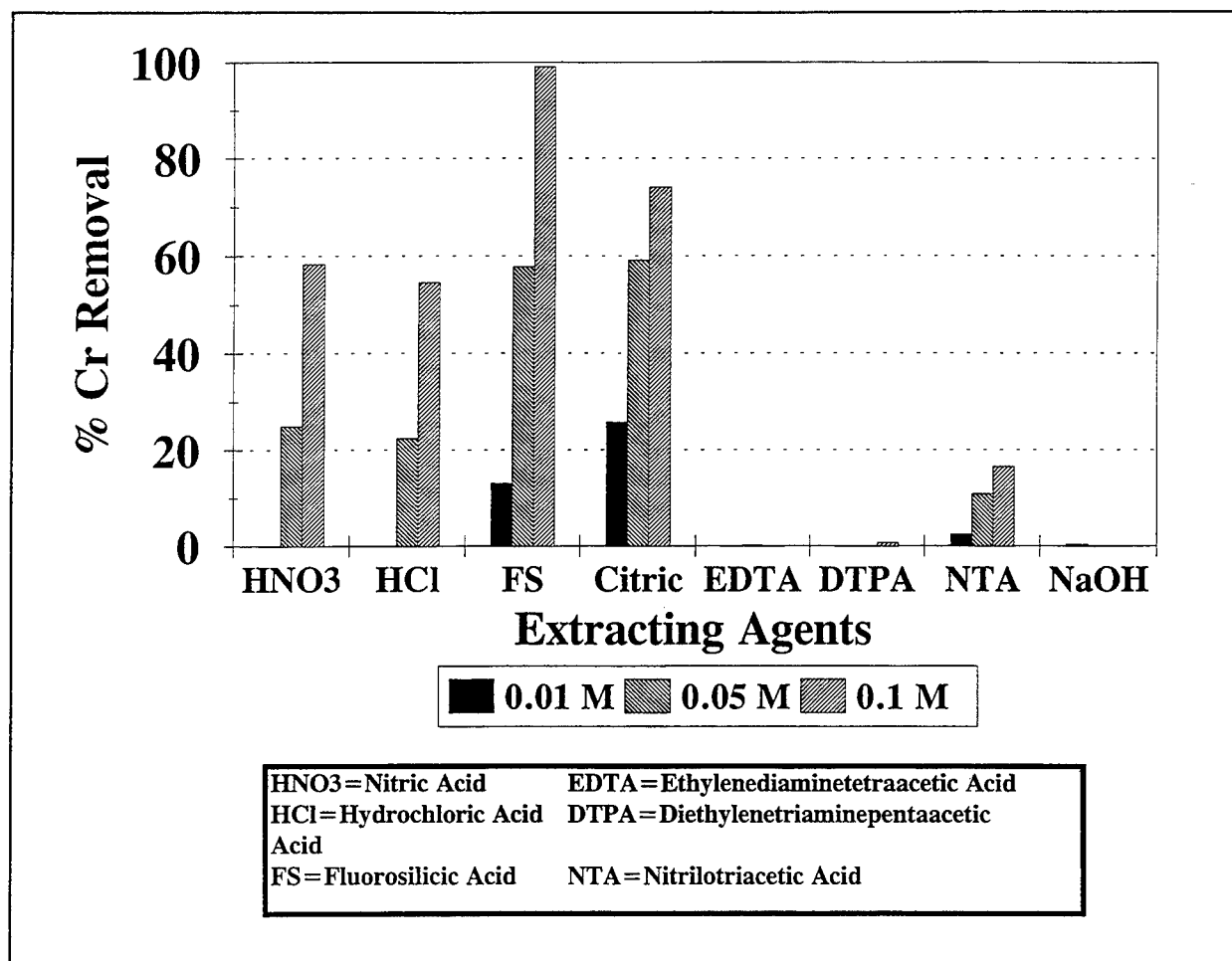


Figure 21. Cr removal efficiency versus extracting agents for LAAP Site 2 soil

studies. The list of soils was narrowed from eight to four and included the Umatilla, SE Fort Sites 5-8, LAAP Site 2, and WES spiked soils. This shortened the number of required tests, while still maintaining soils with a variety of physical and chemical characteristics.

The list of extracting agents was also narrowed to four, and the concentrations for these extracting agents were narrowed to one. Many of the soils contained more than one metal contaminant; therefore, the selected extracting agents were desired to be effective at removing all three of the metals. While HNO₃ and HCl generated similar removal efficiencies for the three metals studied and both are strong acids, only HNO₃ was selected for further study. The remaining extracting agents selected were citric acid, EDTA, and DTPA. A concentration of 0.05 M was chosen as generally the most efficient and effective concentration for use in further tests.

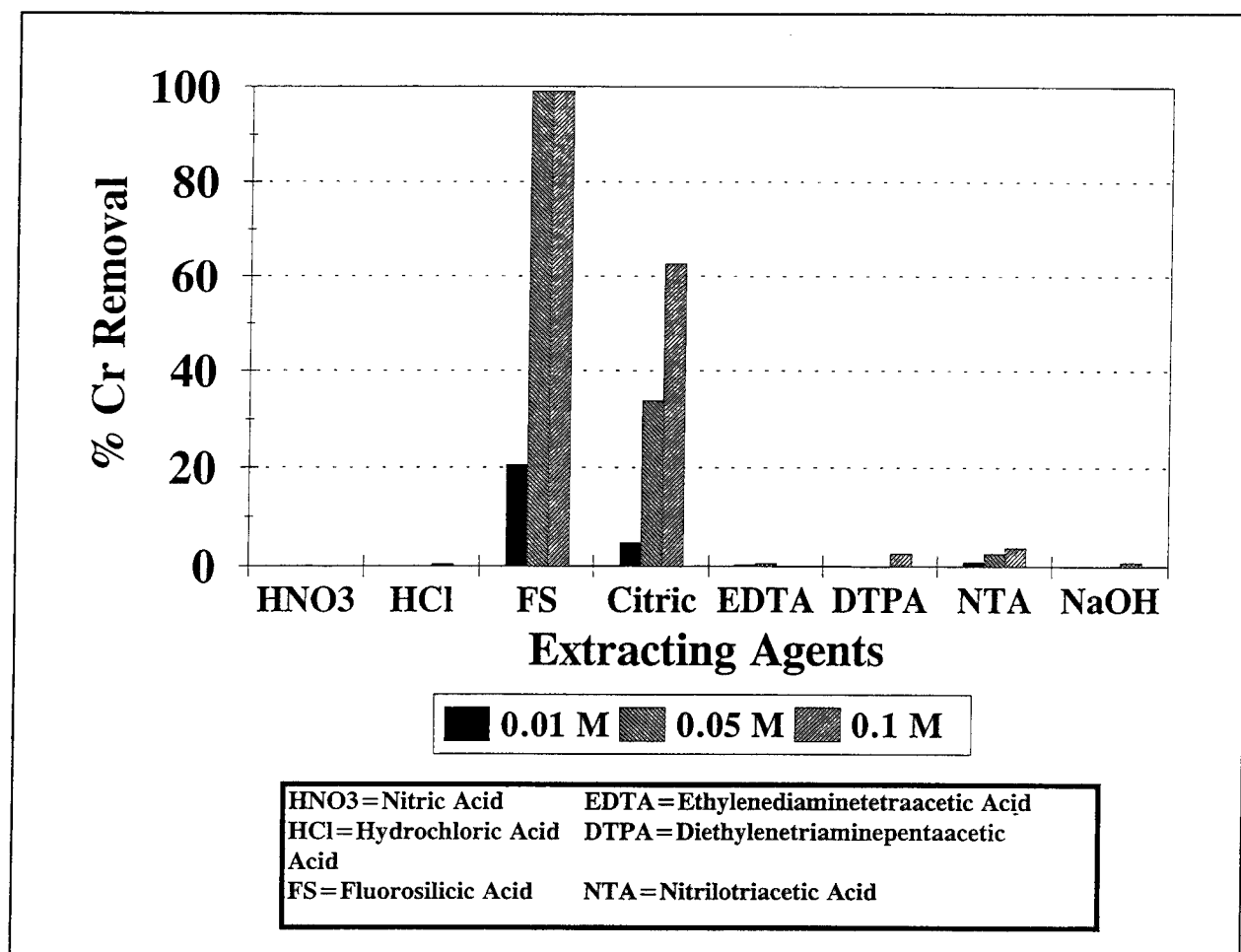


Figure 22. Cr removal efficiency versus extracting agents for WES spiked soil

Steady-state test

Previously conducted investigations studying metal extraction do not agree regarding the reaction time for contaminated soils and extracting agents to reach chemical steady-state. The steady state times ranged from 1 hr for the removal of Pb from soil using EDTA (Peters and Shem 1991) to 12 hr for the removal of Cd from marine sediment (Trefry and Metz 1984). As a result, a study to investigate the specific reaction time required to establish steady state for each of the selected soils and extracting agents was necessary. Using the steady-state information from these tests, an accurate and efficient retention time can be selected for the counter-current metal extraction system.

As indicated in Figures 23-29, extraction of Pb, Cd, and Cr over 30 hr using the selected soils and reagents generally followed first-order kinetics. However, the rate at which the reactions occurred varied somewhat with soil, reagent, and contaminant type. Two methods were developed to quantify the variable reaction rates and times to reach steady state. Since generally the rate of metal extraction was rapid during

Table 25
Statistical Analysis Output for Extractant Effectiveness Test, Cr-Contaminated Soils

Analysis of Variance Procedure Class Level Information					
Class	Levels		Values		
Soil	3		LAAPS1, LAAPS2, WES		
Ext	8		HNO ₃ , HCl, FS, Citric, EDTA, DTPA, NTA, NaOH		
Conc	3		0.01, 0.05, 0.1		
Number of observations in data set = 72					
Dependent variable: Cr					
Source	DF	ANOVA SS	Mean Square	F Value	Pr > F
Soil	2	886.1603	443.0801	1.49	0.2332
Ext	7	21637.9182	3091.1304	10.41	0.0001
Conc	2	4832.3003	2416.1501	8.13	0.0007
Waller-Duncan K-ratio T test for variable: Cr					
Note: This test minimizes the Bayes risk under additive loss and certain other assumptions.					
K ratio = 100 df = 60 MSE = 297.0491 F = 10.40613					
Critical Value of T = 1.86485					
Minimum Significant Difference = 15.151					
Means with the same letter are not significantly different.					
Waller Grouping		Mean	N	Ext	
A		53.722	9	FS	
	B	38.300	9	Citric	
		19.256	9	HNO ₃	
	C	16.622	9	HCl	
	C	13.400	9	NTA	
	C	5.789	9	NaOH	
		1.722	9	EDTA	
		1.211	9	DTPA	
K-ratio = 100 df = 60 MSE = 297.0491 F = 8.133841					
Critical Value of T = 1.90320					
Minimum Significant Difference = 9.4691					
(Continued)					

Table 25 (Concluded)								
Means with the same letter are not significantly different.								
Waller Grouping		Mean	N	Conc				
A		28.279	24	0.1 M				
A		19.700	24	0.05 M				
	B	8.279	24	0.01 M				
Duncan's Multiple Range Test for Variable: Cr								
Note: This test controls the Type I comparisonwise error rate, not the experimentwise error rate.								
Alpha = 0.05 df = 60 MSE = 297.0491								
Number of Means		2	3	4	5	6	7	8
Critical Range		16.25	17.10	17.65	18.06	18.37	18.62	18.83
Means with the same letter are not significantly different.								
Duncan Grouping		Mean	N	Ext				
A		53.722	9	FS				
A		38.300	9	Citric				
	B	19.256	9	HNO ₃				
	B	16.622	9	HCl				
	B	13.400	9	NTA				
	B	5.789	9	NaOH				
	B	1.722	9	EDTA				
	B	1.211	9	DTPA				
Alpha = 0.05 df = 60 MSE = 297.0491								
Number of Means		2	3					
Critical Range		9.95	10.47					
Means with the same letter are not significantly different								
Duncan Grouping		Mean	N	Conc				
A		28.279	24	0.1 M				
A		19.700	24	0.05 M				
	B	8.279	24	0.01 M				

the first 3 hr of contact, simple linear regression was conducted on the first five points of each data set to determine a slope or "rate of reaction" (See Figure 23 for example plot). Second, 90 percent of the maximum extraction efficiency was selected to represent a reasonable extraction efficiency; therefore, the time to reach this removal efficiency was determined to be the time at which the system reached steady state, thus providing a basis for comparison. The raw data for this testing is presented in Appendix D.

Table 26 Most Effective Extracting Agents and Concentrations for Selected Metals		
Contaminant Metal	Best Reagents	Optimal Concentration, M
Pb	HCR HNO ₃ DTPA Citric Acid	0.05
Cd	Citric Acid HCl HNO ₃ EDTA	0.05
Cr	Citric Acid	0.05

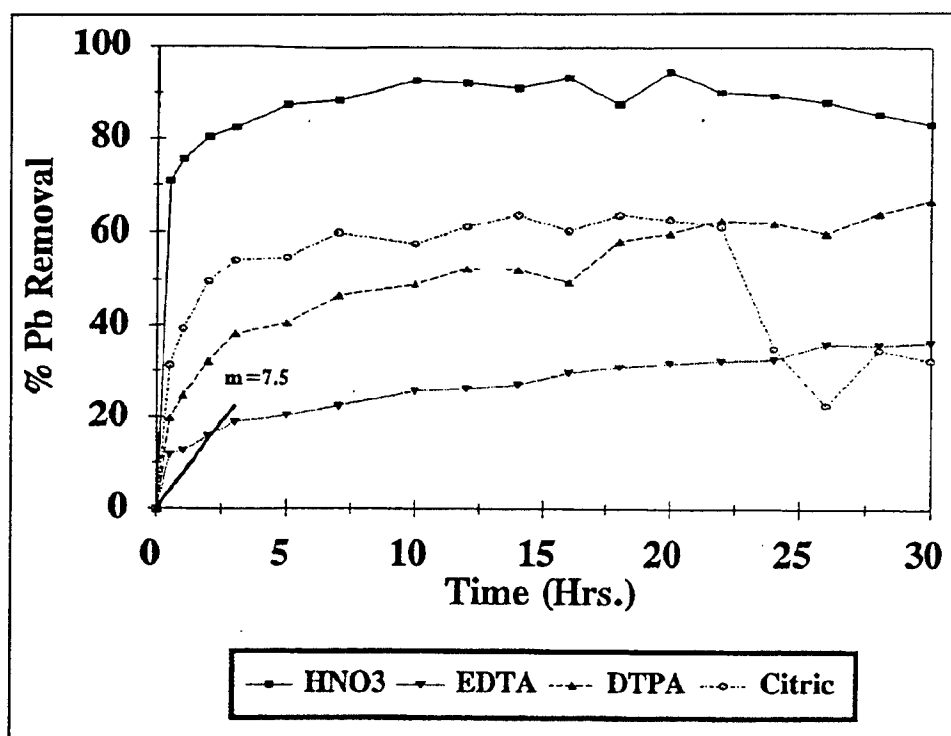


Figure 23. Steady-state desorption test for Pb-contaminated Umatilla soil

Pb Steady-State Results

The steady-state tests for the Pb-contaminated soils including the Umatilla, SE Fort, and WES spiked soils are presented in Figures 23-25, respectively. The rate of extraction during the first 3 hr in the WES spiked soil was much more rapid than the rates in the two contaminated soils exposed to the natural environment as illustrated in Table 27 by the larger slope (m). This was expected as a result of the fact

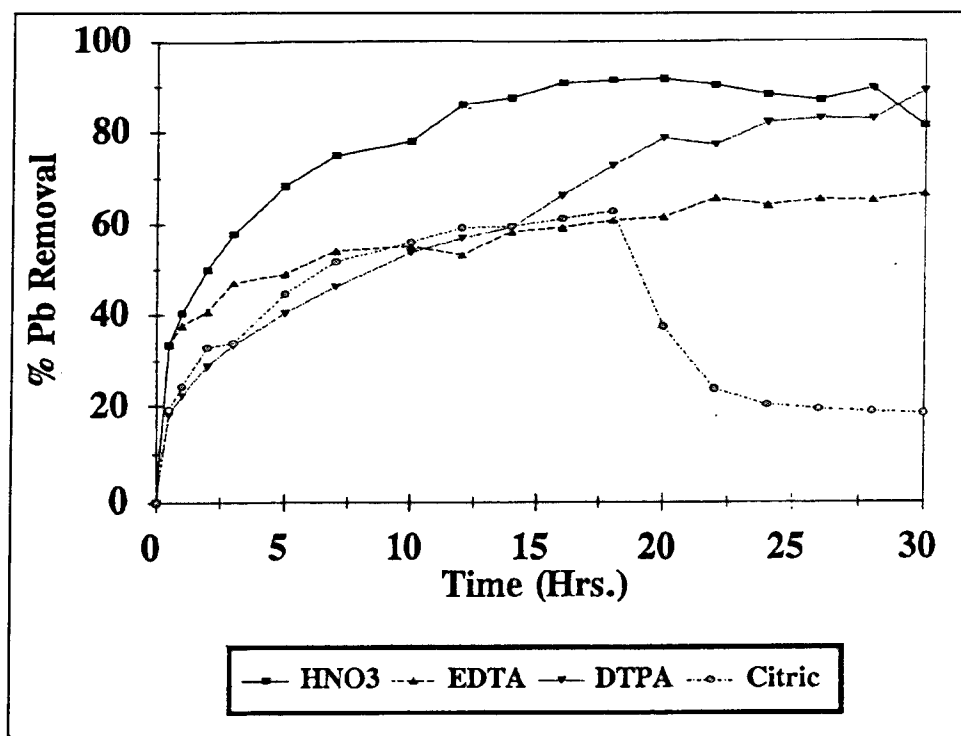


Figure 24. Steady-state desorption test for Pb-contaminated SE Fort soil

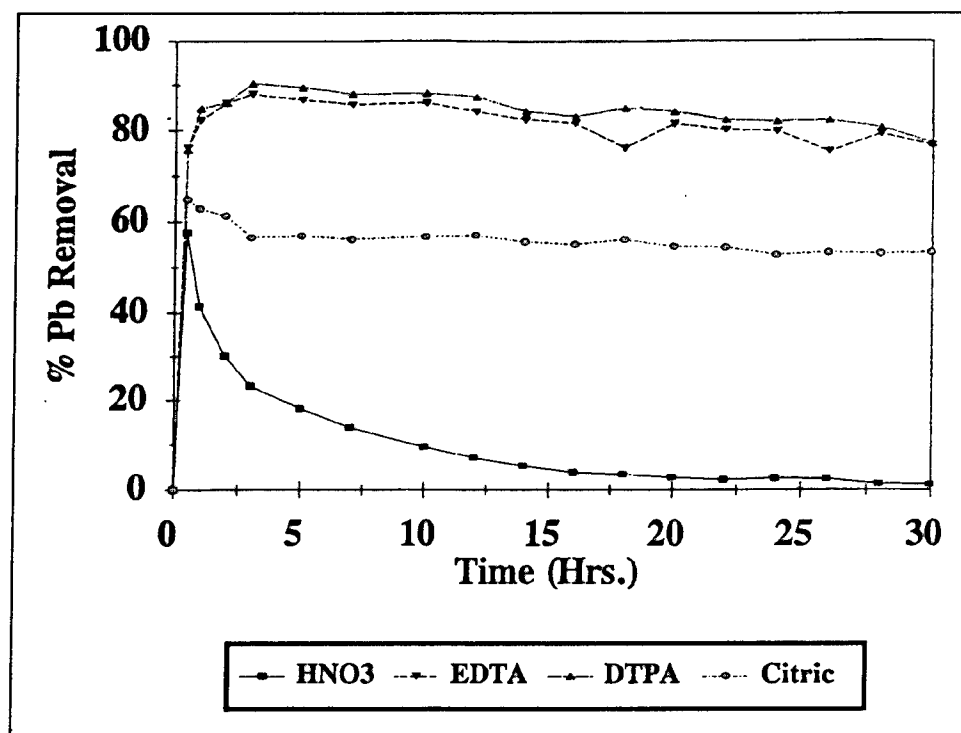


Figure 25. Steady-state desorption test for Pb-contaminated WES spiked soil

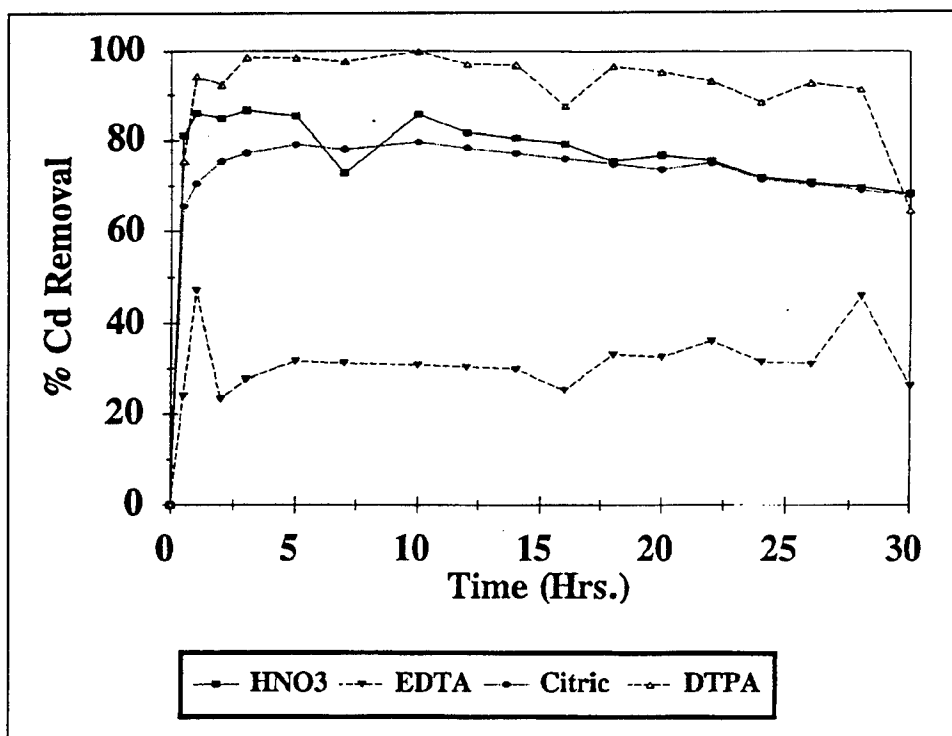


Figure 26. Steady-state desorption test for Cd-contaminated LAAP soil

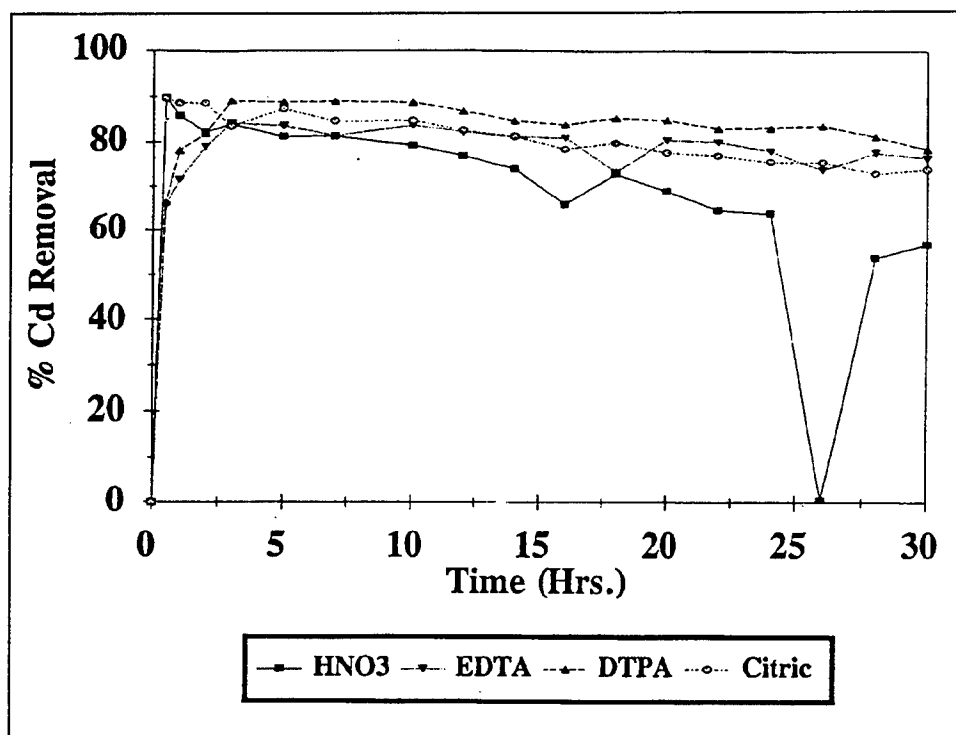


Figure 27. Steady-state desorption test for Cd-contaminated WES spiked soil

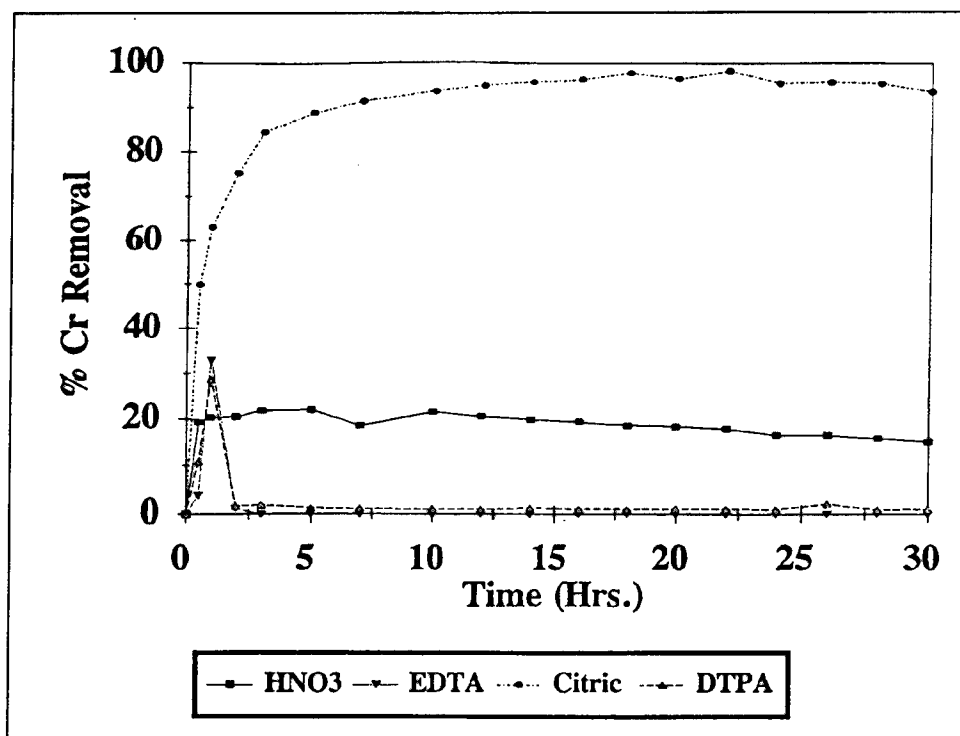


Figure 28. Steady-state desorption test for Cr-contaminated LAAP soil

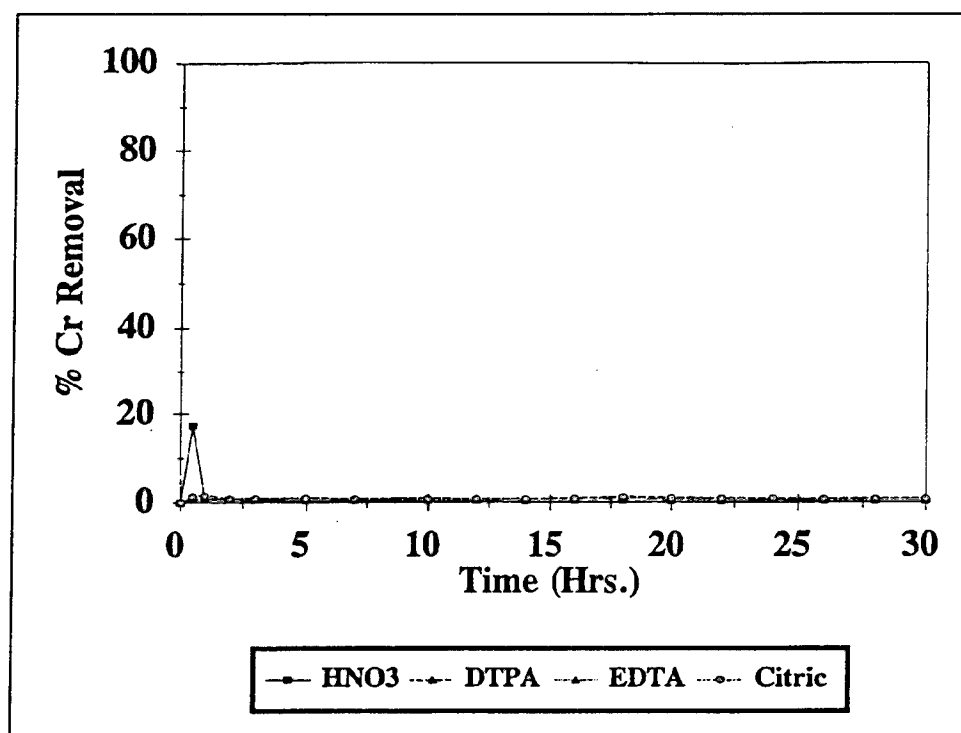


Figure 29. Steady-state desorption test for Cr-contaminated WES spiked soil

Table 27 Reaction Rates and Times for Pb-Contaminated Soils				
Soil Type	Reagent	Regression Slope (m) Over First 3 Hr of Contact Time	90 Percent of Maximum Removal Efficiency percent	Time to Reach 90 Percent of Maximum Removal Efficiency, hr
Umatilla	HNO ₃	36.4	85	5
Umatilla	EDTA	7.5	33	26
Umatilla	DTPA	15.0	60	20
Umatilla	Citric Acid	22.2	57	7
SE Fort	HNO ₃	23.2	82	12
SE Fort	EDTA	19.5	60	18
SE Fort	DTPA	13.3	80	24
SE Fort	Citric Acid	14.1	57	12
WES Spiked	HNO ₃	14.0	52	0.5
WES Spiked	EDTA	39.0	79	1
WES Spiked	DTPA	39.7	81	1
WES Spiked	Citric Acid	27.2	58	0.5

that the contaminants were exposed to the spiked soil for a much shorter period of time than for the nonspiked soils. The exposure of the Umatilla and SE Fort soils to weathering, reduction-oxidation processes, etc., most likely resulted in the Pb being more tightly sorbed to the soil surface and thus more difficult to remove during the initial 3 hr of contact time.

Regardless of the soil type, HNO₃ had the most rapid rate of Pb extraction during the first 3 hr of reaction time, with the exception of the WES spiked soil. As illustrated by Figure 23, maximum extraction using HNO₃ was reached quickly (0.5 hr), after which the amount of successfully extractable Pb rapidly decreased (the next 10-15 hr). The decrease in Pb solubilization for the WES spiked soil may be attributed to neutralization of the acid that had occurred as a result of the increasing contact time. This increase in pH may have a slight effect on Pb solubility. For the WES spiked soil, the pH of the initial solution was 1.0. After 0.5 hr of contact time, the pH of the slurry was 4.67 and steadily rose to 6.08 by the end of the 30-hr test. For the majority of the soils, the rate of reaction (or slope over the initial 3 hr of contact time) was inversely correlated with the time necessary to reach the 90-percent extraction efficiency. For example, 90-percent Pb extraction was reached more rapidly using HNO₃ than using the other reagents, and as illustrated in Table 27, the time to achieve optimal Pb-removal efficiency was 5, 12, and 0.5 hr for the Umatilla, SE Fort, and WES spiked, respectively.

For the Pb contaminant, the removal efficiency dramatically decreased after 20 hr in both the Umatilla and SE Fort desorption tests using citric acid. No significant changes in the pH were recorded in either of the tests; however, citric acid may have undergone decarboxylation in which one or more of the carboxyl groups binding the Pb cation was transformed to CO₂, resulting in reentrainment of the Pb in the soil. Further studies are needed to verify the decarboxylation phenomenon. No decrease in metal removal efficiency was observed in the desorption test using the WES spiked soil and citric acid. Discounting the drop in Pb solubility after 20 hr, an interim steady-state condition using citric acid was reached in 7, 12, and 0.5 hr for the Umatilla, SE Fort, and WES spiked soils, respectively.

Both EDTA and DTPA reacted similarly over the range of Pb-contaminated soils. In the WES spiked soil (Figure 25), both EDTA and DTPA had similar rates of reaction over the first 3 hr of reaction time. Also, the time to reach steady state in the WES spiked soil for Pb was 1 hr for both reagents. In the Umatilla soil (Figure 23), Pb-removal efficiency using both EDTA and DTPA appeared to steadily increase throughout the duration of the test. Thirty hours may not be a sufficient amount of time for either of these systems to reach a steady-state condition, but this rate of increase is minimal.

Cd Steady-State Results

Desorption tests for the Cd-contaminated, LAAP and WES spiked soils are shown in Figures 26 and 27, respectively. As shown in Table 28, the rate of reaction for Cd was generally rapid and typically higher than the reaction rates for the Pb-contaminated soils (Table 27). In this test, Cd was removed more easily from

Table 28
Reaction Rates and Times for Cd-Contaminated Soils

Soil Type	Reagent	Regression Slope (m) Over First 3 Hr of Contact Time	90 Percent of Maximum Removal Efficiency percent	Time to Reach 90 Percent of Maximum Removal Efficiency, hr
LAAP	HNO ₃	39.0	78	0.5
LAAP	EDTA	12.2	41	28
LAAP	DTPA	43.0	72	2
LAAP	Citric Acid	34.1	90	1
WES Spiked	HNO ₃	38.4	81	0.5
WES Spiked	EDTA	36.1	76	2
WES Spiked	DTPA	38.0	80	2
WES Spiked	Citric Acid	39.4	81	0.5

contaminated soil than either Pb or Cr; therefore, it was expected that the reaction rate during the first 3 hr of contact would be higher. However, the rates of reaction for the initial 3 hr of contact time of the WES spiked/EDTA and WES spiked/DTPA desorption tests contradicted this general trend. The rates were slightly higher for the removal of Pb than for the removal of Cd. Since most of the reaction rates were rapid, the majority of the accompanying times to reach 90-percent steady state were in the range of 30 min to 2 hr, with the exception of the LAAP/EDTA system. In comparing soils exposed to the natural environment, the time to reach steady state for Cd removal was much shorter than the time to reach steady state for Pb removal. No differences in the time to reach steady state for Cd versus Pb were observed in the spiked soil.

With the exception of the LAAP/EDTA system, removal efficiency slowly decreased after a rapid rise during the first 3-5 hr of contact time for the Cd desorption tests. No major changes in the pH of the systems were observed during extraction testing except for the WES spiked/ HNO_3 system as discussed earlier. Since the trend was prevalent in most of the systems, future studies are now being proposed to investigate the cause of the gradual reduction of soluble Cd over time.

Cr Steady-State Results

Desorption tests for the Cr-contaminated LAAP and WES spiked soils are presented in Figures 28 and 29, respectively. Only citric acid and HNO_3 were able to successfully remove substantial amounts of Cr from the LAAP soil, while none of the reagents were able to remove Cr from the WES spiked soil. The Cr contained in both of the soils was typically in the highly insoluble trivalent (+3) state. As a result, very few conclusions can be drawn regarding steady-state conditions for the removal of Cr. Citric acid was able to rapidly remove Cr from the LAAP soil during the first 3 hr of contact time. For citric acid, the reaction rate was higher for Cr removal than for Pb removal. As a result of rapid extraction, the time for the LAAP/citric acid system to reach steady state was only 5 hr (Table 29). It should also be noted that unlike Umatilla and SE Fort soil desorption tests involving citric acid and Pb, readsorption of the Cr onto the soil did not occur. This difference may be attributed to the structure of citric acid. The organic acid has one hydroxyl and three carboxyl functional groups that are capable of ionic bonding with metal cations. In a tetrahedral arrangement, Cr^{+3} may be tightly bound to the three carboxyl groups, whereas Pb^{+2} may only be bound by two of the functional groups. As a result, a breakdown of the bond with Cr^{+3} is much less likely than a breakdown of the bond with Pb^{+2} .

HNO_3 was the only other reagent capable of the desorption of Cr from the LAAP soil. Unlike citric acid, the HNO_3 rate of reaction for Cr removal for the first 3 hr of contact time was considerably less than the HNO_3 rate for Pb removal.

Table 29
Reaction Rates and Times for Cr-Contaminated Soils

Soil Type	Reagent	Regression Slope (m) Over First 3 Hr of Contact Time	90 Percent of Maximum Removal Efficiency, percent	Time to Reach 90 Percent of Maximum Removal Efficiency, hr
LAAP	HNO ₃	9.6	20	1
LAAP	EDTA	2.6	30	1
LAAP	DTPA	3.1	26	1
LAAP	Citric Acid	34.6	88	5
WES Spiked	HNO ₃	0.9	16	0.5
WES Spiked	EDTA	0.4	1	1
WES Spiked	DTPA	0.5	2	1
WES Spiked	Citric Acid	0.5	1	0.5

For the three desorption tests including LAAP/EDTA, LAAP/DTPA, and WES spiked/HNO₃, Cr extraction was rapid during the first hour and was followed by a sharp decrease in the following 1-2 hr. No explanation for this trend could be found. Further investigation is therefore needed to determine the cause of the shifting Cr equilibrium between the solid and liquid phases.

5 Conclusions

Laboratory studies were conducted to investigate the optimal operating conditions of the continuous-flow, pilot-scale, countercurrent metal extraction system. These studies included a solid-to-liquid ratio test, an extractant effectiveness test, and an equilibrium test. Based on the results of these studies, the following conclusions were drawn.

- a. Treatability studies must be conducted on contaminated material before initiating a pilot-scale or full-scale soil washing/chemical extraction process to determine influential factors as soil type, major contaminant of interest, optimal reagent and concentration, and optimal contact or retention time.
- b. The extraction of metals from contaminated soil using an extracting agent is significantly affected by decreasing the solid-to-liquid ratio from 0.5 to 0.005. Therefore, for this study to maximize the volume of soil treated per unit volume of extracting agent, a solid-to-liquid ratio of 0.05 should be used.
- c. Metal extraction efficiency depends on the type of metal contaminant being extracted. The ease of removal of the three metals in this study is shown below (Cd = easiest to remove):

$$Cd > Pb >> Cr$$

- d. Fluorosilicic acid and HCl are the most effective extracting agents for the removal of Pb from soils, followed closely by HNO_3 , NTA, and DTPA.
- e. HNO_3 , NTA, and citric acid are the most effective extracting agents for the removal of Cd from soils.
- f. Fluorosilicic acid and citric acid are the most effective extracting agents for the removal of Cr from soils.
- g. Contrary to expected findings, an increase in reagent concentration does not necessarily result in an increase in metal removal efficiency. For this

investigation, the most efficient and effective extracting agent concentration is 0.05 M for the soils studied.

- h.* The specific reaction time to reach chemical equilibrium for metal-contaminated soils and extracting agents ranges from 30 min to greater than 28 hr. The time to reach chemical equilibrium is dependent on the soil type, the metal contaminant, and the extracting agent.
- i.* Rapid extraction of all three metals is generally observed in the initial 3 hr contact time between contaminated soil and reagent.
- j.* As expected, the time to reach chemical equilibrium or maximum extraction efficiency is much more rapid in the WES spiked soil than in the soils exposed to the environment.

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Appendix A

Methods for Batch Studies

Countercurrent Method 1 Solid-To-Liquid Batch Test

Scope and application

This method is a metal extraction procedure used to determine the optimal solid-to-liquid ratio between soil and solvent and the time at which no more metal is extracted from the soil by the solvent (equilibrium). It should be noted that in similar tests, the optimal solid-to-liquid ratio is 0.05, and the maximum time needed to achieve total metal extraction is 24 hr. These values should be used as initial guidelines when performing this test. Three solid-to-liquid ratios were initially tested: 0.05, 0.2, and 0.5. Two soils and two solvents were tested with one solvent being a strong acid and the other being a chelating agent. Three concentrations of each solvent were tested: 0.01 M, 0.05 M, and 0.1 M. Samples were drawn at two time intervals: 24 hr and 30 hr.

Summary of method

Three soil samples (<2 mm homogenized) were prepared weighing 15, 60, and 150 g (dry weight), respectively. The samples were placed in a container with approximately 300 ml of solvent. The soil and solvent were tumbled for 24 hr, after which approximately 100 ml of solvent with extracted metal was filtered and analyzed. The containers were then placed back on the tumbling apparatus for an additional 6 hr (totaling 30 hr), and another 100 ml of solvent with extracted metal was filtered and analyzed. Once analyzed, determinations were made as to whether additional tests needed to be performed (for example, narrowing focus of solid-to-liquid ratios to 0.05 and smaller, or increasing the time needed to reach equilibrium).

Apparatus and materials

500-ml Nalgene HDPE bottles.
125-ml Nalgene HDPE bottles.
Strapping Tape.
Whatman GF/F filters (47-mm diam).
Millipore Type HA 0.45- μ m filters (47-mm diam).
Tumbling (end-over-end) apparatus.
Millipore Sterifil Aseptic Filtration System.
Gilson No. 10, 2-mm sieve.
Beckman 45 pH meter.

Reagents

Distilled, deionized water (DDI).
Concentrated hydrochloric acid (HCl), reagent grade (or another strong acid).
Ethylenediaminetetraacetic acid, calcium disodium salt hydrate, 98 percent (or another chelating agent).
Concentrated nitric acid (HNO₃), reagent grade.

Procedure

Sieve bulk soil to less than 2 mm using a Gilson No. 10 sieve. After sieving, completely and thoroughly homogenize the soil. For each soil-solvent-concentration combination tested, weigh out 15, 60, and 150 g (dry weight), respectively, to the nearest 0.01 g and place each in a precleaned, acid-washed 500-ml Nalgene HDPE bottle.

Add 300 ml of solvent to each bottle to be tested. Seal the bottle tightly, and tape the bottle top clockwise using commercial strapping tape to avoid leakage. Note that the number of tests run will be a factor of the number of soils tested, the number of solvents tested, the number of concentrations of solvents, and the number of solid-to-liquid ratios tested (See schematic attached).

Place the bottle(s) on the tumbling apparatus and let tumble for 24 hr at approximately 18 ± 2 rpm.

Remove bottle(s) from tumbler and allow to settle for 10 min. Place a Whatman GF/F 47-mm filter on top of Millipore Sterifil Aseptic Filtration System membrane. Sample rinse the Millipore Sterifil Aseptic Filtration System by pouring in approximately 10 ml of solution and attach to vacuum source. After discarding the sample rinse, filter 50-100 ml of solution through filtration system.

If filtered solution is cloudy, refilter using Millipore Type HA 0.45- μ m filter.

Sample rinse 125-ml Nalgene HDPE bottle with 10 ml of filtered solution. Pour remainder of filtered solution into rinsed 125-ml bottle. Measure and record pH of

solution with Beckman 45 pH meter. If pH is greater than 2, add concentrated nitric acid to solution until pH is less than 2 for preservation. Place bottle with solution into storage at 4 °C until analysis can be performed.

Recap samples and seal tightly with strapping tape. Place the bottle(s) back into the tumbling apparatus and tumble for another 6 hr giving a total of 30 hr tumbling time.

Remove bottle(s) from tumbler and repeat steps as necessary.

Calculations

Concentrations of metals in filtered solution were analyzed using flame atomic absorption spectrophotometry. Results were reported in milligrams of metal per gram of soil used. Below is an example:

Amount of soil used = 15 g

Amount of solvent = 300 ml

Concentration of metal in solution after AAS analysis = 200 mg/l

Result in milligram/gram soil = $(200 \text{ mg/l}) \cdot (0.3 \text{ l}) / (15 \text{ g}) = 4 \text{ mg of metal per gram of soil used}$

Quality control

Blanks were run for each solvent used. Carry the blanks through all the stages previously mentioned.

Duplicates were run periodically to ensure accuracy of results.

Countercurrent Method 2 Extractant Effectiveness Batch Test

Scope and application

This method is a metal extraction procedure designed to determine the most effective extractants and concentrations to use with various soils. Similar extraction tests have shown the following reagents to be effective at extracting heavy metals from soils in solution: nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), nitric acid (HNO₃), hydrochloric acid (HCl), citric acid, fluorosilicic acid, and sodium hydroxide (NaOH). Three concentrations of each of these extracting agents were tested: 0.01 M, 0.05 M, and 0.1 M. Solid-to-liquid ratio and tumbling time were predetermined using Countercurrent Method 1.

Summary of method

Soil samples (<2 mm homogenized) of each soil to be tested were prepared weighing 5 g each (dry weight) if S:L = 0.05 from Countercurrent Method 1. Each sample was placed in a bottle, and approximately 100 ml of extracting agent was added. The soil and extracting agent were tumbled for 30 hr after which approximately 50-75 ml of extracting agent with metal was filtered and analyzed. Once analyzed, percent removal of each metal for the various extracting agents was determined provided a total metals analysis of each soil had been done (USEPA Method 3050).

Apparatus and materials

250-ml centrifuge bottles.
125-ml Nalgene HDPE bottles.
Strapping tape.
Sorvall Superspeed centrifuge model SS-3 or equivalent.
Millipore Sterifil Aseptic Filtration System.
Millipore Type HA 0.45 μ m filters (47-mm diam).
Tumbling (end-over-end) apparatus.
Gilson No. 10, 2-mm sieve or equivalent.
Beckman 45 pH meter or equivalent.
AND Model FX-3000 Balance correct to two decimal places, or equivalent.

Reagents

Distilled, deionized water (DDI).
Hydrochloric acid (HCl), reagent grade.
Nitric acid (HNO₃), reagent grade.
Citric acid, 99+-percent pure.
Sodium hydroxide (NaOH), 97+-percent pure.
Nitrilotriacetic acid (NTA), disodium salt, 99+-percent pure.
Ethylenediaminetetraacetic acid (EDTA), calcium disodium salt hydrate 98-percent pure.
Diethylenetriaminepentaacetic acid (DTPA), calcium trisodium salt hydrate 97-percent pure.
Fluorosilicic acid.

Procedure

Sieve bulk soil to less than 2 mm using a Gilson No. 10 sieve. After sieving, completely and thoroughly homogenize the soil. For each soil-extracting agent-concentration combination tested, weigh out 5 g (dry weight) to the nearest 0.01 g using AND Model FX-3000 balance and place each in a precleaned, acid-washed 250-ml centrifuge bottle.

Add 100 ml of extracting agent to each bottle to be tested. Seal the bottle tightly, and tape the bottle top clockwise using commercial strapping tape to avoid leakage. Note that the number of tests run will be a function of the number of soils tested and the number of extracting agents tested.

Place the bottle(s) in the tumbling apparatus and let tumble for 30 hr at 18 rpm.

Remove bottle(s) from tumbler. Place bottle(s) in Sorvall Superspeed SS-3 table-top centrifuge (six bottle rack). Centrifuge for 30 min at approximately 15,000 rpm.

Remove bottle(s) from centrifuge. Place a Millipore Type HA 0.45 μm filter on top of Millipore Sterifil Aseptic Filtration System membrane. Sample rinse the Millipore Aseptic Filtration System by pouring in approximately 10 ml of solution from bottle and attach to vacuum source. After discarding the sample rinse, filter 50-75 ml of solution through filtration system.

Sample rinse 125 ml Nalgene HDPE bottle with 10 ml of filtered solution. Pour remainder of filtered solution into rinsed 125-ml bottle. Measure and record pH of solution using Beckman 45 pH meter. If pH is greater than 2, add concentrated nitric acid to solution until pH is less than 2 for preservation (usually 1 ml is sufficient). Place bottle into storage at 4 °C until analysis can be performed.

Calculations

Concentrations of metals in filtered solution were analyzed using flame atomic absorption spectrophotometry. Results were reported in percent removal of metal using the value for concentration of metal in solution and the value for concentration of metal in bulk soil from total metals analysis procedure. Below is an example:

Amount of soil used = 5 g
Amount of extracting agent = 100 ml
Amount of metal in soil from total metals analysis = 30,000 mg/kg
Concentration of metal in solution after AAS analysis = 558 mg/l

(1) Calculate milligrams of metal per gram of soil used in test.

$$\begin{aligned} &= (558 \text{ mg/l}) * (0.1 \text{ l}) / (5 \text{ g}) \\ &= 11.16 \text{ mg/g soil} \end{aligned}$$

(2) Calculate milligrams of metal per gram of bulk soil.

$$\begin{aligned} &= (30,000 \text{ mg/kg}) * (1 \text{ kg} / 1,000 \text{ g}) \\ &= 30 \text{ mg/g of bulk soil.} \end{aligned}$$

(3) Calculate percent removal.

$$\begin{aligned} &= (11.16 \text{ mg/g}) / (30 \text{ mg/g}) * 100 \\ &= 37.2\text{-percent removal from soil tested} \end{aligned}$$

Quality control

Duplicates were run periodically to ensure accuracy of results.

Countercurrent Method 3 Equilibrium Batch Test

Scope and application

This method is a metal extraction procedure designed to determine the contact time necessary for the extracting agent and soil to reach equilibrium, which is defined to be zero net change in the concentration of metals in the extracting agent and in the concentration of metals in the soil. Four extracting agents were determined using Countercurrent Method 2: EDTA, DTPA, Nitric acid (HNO_3), and Citric acid. Four soils were determined using Countercurrent Method 2: Polk 5, 6, 7, 8, LAAP 16, 17, 18, Umatilla, and HWRIC Spk. Only one concentration was tested (0.05M) as determined by Countercurrent Method 2. Samples were drawn at the following time intervals: 0.5, 1, 2, 3, 5, 7, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, and 30 hr for a total of 17 samples for each extracting agent-soil combination.

Summary of method

Soil samples (<2-mm homogenized) of each soil to be tested were prepared weighing 45 g each (dry weight) if S:L = 0.05 from Countercurrent Method 1. Each sample was placed in a 1-l bottle, and approximately 900 ml of extracting agent was added. The soil and extracting agent were tumbled for 30 min after which approximately 12 ml of extracting agent with metal was filtered using syringe filtration. Each sample was then analyzed. The same procedure was followed for the remaining 16 samples. Once analyzed, percent removal of each metal for the various extracting agents at each time was determined provided a total metals analysis of each soil had been done (USEPA Method 3050).

Apparatus and materials

- 1-l Nalgene HDPE bottles.
- 125-ml Nalgene HDPE bottles.
- Strapping tape.
- Sorvall Superspeed centrifuge model SS-3 or equivalent.
- Tumbling (end-over-end) apparatus.
- Gilson No. 10, 2-mm sieve or equivalent.
- Beckman 45 pH meter or equivalent.
- AND Model FX-3000 Balance correct to two decimal places, or equivalent.
- Terumo 10-cc luer lock-tip disposable syringes or equivalent.
- Gelman 0.45 μm 25-mm DM Metricel membrane filters.
- Gelman 25-mm Easy Pressure syringe filter holder.
- 50-ml PPCD Oak Ridge Centrifuge tubes or equivalent.

Reagents

Distilled, deionized water (DDI).

Nitric acid (HNO_3), reagent grade.

Citric acid, 99+-percent pure.

Ethylenediaminetetraacetic acid (EDTA), calcium disodium salt hydrate, 98 percent.

Diethylenetriaminepentaacetic acid (DTPA), calcium trisodium salt hydrate, 97 percent.

Procedure

Sieve bulk soil to less than 2 mm using a Gilson No. 10 sieve. After sieving, completely and thoroughly homogenize the soil. For each soil-extracting agent combination tested, weigh out 45 g (dry weight) to the nearest 0.01 g using AND Model FX-3000 balance and place each in a pre-cleaned, acid-washed 1 l Nalgene HDPE bottle.

Add 900 ml of extracting agent to each bottle. Seal the bottle tightly and tape the bottle top clockwise using commercial strapping tape to avoid leakage.

Place the bottle(s) in the tumbling apparatus and let tumble for 30 min at 18 rpm.

Remove bottle(s) from tumbler. Pour approximately 30 ml of solution into clean PPCD Oak Ridge centrifuge tube. Return bottle(s) to tumbler after sealing and tumble for another 30 min (total contact tumbling time = 1 hr). Place centrifuge tube(s) in Sorvall Superspeed Model SS-3 centrifuge for 20 min at 15,000 rpm.

Remove centrifuge tube(s) from centrifuge. Draw 12 ml of solution from centrifuge using Terumo Luer Lock Tip syringe. Place Gelman Easy Pressure filter holder containing Gelman 0.45 μm filter on end of syringe. Depress syringe and pump filtered solution into 125-ml Nalgene HDPE bottle. Measure and record pH of solution using Beckman 45 pH meter. If pH is greater than 2, add concentrated nitric acid to solution until pH is less than 2 for preservation (usually 1 ml is sufficient). Place bottle into storage at 4 °C until analysis can be performed.

Previous steps should be performed at the following time intervals: 0.5, 1, 2, 3, 5, 7, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30 hr. Note that these times represent total contact tumbling time.

Calculations

Concentrations of metals in filtered solution were determined using flame atomic absorption spectrophotometry. Results were reported in percent removal of metal using value for concentration of metal in solution and the value for concentration of metal in bulk soil from total metals analysis. Below is an example:

Amount of soil used = 45 g

Amount of extracting agent = 900 ml

Amount of metal in soil from total metals analysis = 30,000 mg/kg

Concentration of metal in solution = 558 mg/l

(1) Calculate milligrams of dissolved metal in extract at each time interval per gram of soil used in the test.

$$Value(1) = \frac{mg\ Me}{g\ Soil} = \frac{\left(\frac{mg}{l} \text{ DissolvedMetal} \right) \times (900\ ml) \times \left(\frac{1\ l}{1000\ ml} \right)}{(45\ g)}$$

(2) Calculate milligrams of metal remaining per gram of bulk soil after 30 hr of chemical extraction.

$$Value(2) = \frac{mg\ Me}{g\ Soil} = \left(\frac{mg}{kg} \text{ TotalMetal} \right) \times \left(\frac{1\ kg}{1000\ g} \right)$$

(3) Calculate total amount of metal in the soil (Maximum total dissolved metal + metal remaining in soil after extraction).

$$Value(3) = (\text{Maximum of Value(1)}) + (Value(2))$$

(4) Calculate percent removal.

$$\%Removal = \frac{Value(1)}{Value(3)} \times 100$$

Quality control

Duplicates were run periodically to ensure accuracy of results.

Appendix B

Statistical Analysis for Solid-To-Liquid Ratio Batch Tests

Solid-To-Liquid Ratio Comparison Using Umatilla Soil and EDTA Contacted for 30 Hr

OBS	SLRATIO	CONC	PB
1	0.5	0.01	0.9744
2	0.5	0.05	1.8057
3	0.5	0.1	2.4943
4	0.2	0.01	1.277
5	0.2	0.05	2.0885
6	0.2	0.1	3.0770
7	0.05	0.01	1.4000
8	0.05	0.05	2.7000
9	0.05	0.1	20.9000
10	0.01	0.01	2.9000
11	0.01	0.05	6.0000
12	0.01	0.1	23.1000
13	0.005	0.01	5.1000
14	0.005	0.05	11.8000
15	0.005	0.1	13.9000

Analysis of Variance Procedure Class Level Information

Class	Levels	Values
SLRATIO	5	0.005 0.01 0.05 0.2 0.5
CONC	3	0.01 0.05 0.1

Number of observations in data set = 15

Analysis of Variance Procedure

Dependent Variable: PB

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	6	520.394190	86.732365	3.05	0.0741
Error	8	227.796948	28.474618		
Corrected Total	14	748.191138			
		R-Square	C.V.	Root MSE	PB Mean
		0.695536	80.43098	5.33616	6.63446

Source	DF	Anova SS	Mean Square	F Value	Pr > F
SLRATIO	4	228.747475	57.186869	2.01	0.1862
CONC	2	291.646715	145.823358	5.12	0.0370

Analysis of Variance Procedure

Waller-Duncan K-ratio T test for variable: PB

NOTE: This test minimizes the Bayes risk under additive loss and certain other assumptions.

Kratio = 100 df = 8 MSE = 28.47462 F = 2.008345

Critical Value of T = 2.67298

Minimum Significant Difference = 11.646

Means with the same letter are not significantly different.

Waller Grouping	Mean	N	SLRATIO
A	10.667	3	0.01
A			
A	10.267	3	0.005
A			
A	8.333	3	0.05
A			

A	2.148	3	0.2
A			
A	1.758	3	0.5

Analysis of Variance Procedure

Duncan's Multiple Range Test for variable: PB

NOTE: This test controls the Type I comparisonwise error rate, not the experimentwise error rate

Alpha = 0.05 df = 8 MSE = 28.47462

Number of Means	2	3	4	5
Critical Range	10.05	10.47	10.71	10.85

Means with the same letter are not significantly different.

Duncan Grouping	Mean	N	SLRATIO
A	10.667	3	0.01
A			
A	10.267	3	0.005
A			
A	8.333	3	0.05
A			
A	2.148	3	0.2
A			
A	1.758	3	0.5

Analysis of Variance Procedure

Waller-Duncan K-ratio T test for variable: PB

NOTE: This test minimizes the Bayes risk under additive loss and certain other assumptions.

Kratio = 100 df = 8 MSE = 28.47462 F = 5.12117

Critical Value of T = 2.39643

Minimum Significant Difference = 8.0877

Means with the same letter are not significantly different.

Waller Grouping	Mean	N	CONC
A	12.694	5	0.1
A			
B A	4.879	5	0.05

B			
B	2.330	5	0.01

Analysis of Variance Procedure

Duncan's Multiple Range Test for variable: PB

NOTE: This test controls the Type I comparisonwise error rate, not the experimentwise error rate

Alpha = 0.05 df = 8 MSE = 28.47462

Number of Means	2	3
Critical Range	7.782	8.110

Means with the same letter are not significantly different.

Duncan Grouping	Mean	N	CONC
A	12.694	5	0.1
B	4.879	5	0.05
B			
B	2.330	5	0.01

Solid-to-Liquid Ratio Comparison Umatilla Soil and HCl Contacted for 30 Hr

OBS	SLRATIO	CONC	PBREMV
1	0.5	0.01	0.0011
2	0.5	0.05	0.0000
3	0.5	0.1	0.0150
4	0.2	0.01	0.0000
5	0.2	0.05	0.2000
6	0.2	0.1	3.1900
7	0.05	0.01	0.1000
8	0.05	0.05	19.9000
9	0.05	0.1	23.2000
10	0.01	0.01	15.6000
11	0.01	0.05	23.5000
12	0.01	0.1	22.4000
13	0.005	0.01	22.7000
14	0.005	0.05	19.3000
15	0.005	0.1	31.4000

Analysis of Variance Procedure
Class Level Information

Class	Levels	Values
SLRATIO	5	0.005 0.01 0.05 0.2 0.5
CONC	3	0.01 0.05 0.1

Number of observations in data set = 15

Analysis of Variance Procedure

Dependent Variable: PBREMV

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	6	1662.69818	277.11636	8.64	0.0038
Error	8	256.59053	32.07382		
Corrected Total	14	1919.28870			

R-Square	C.V.	Root MSE	PB Mean
0.866310	46.80318	5.66337	12.1004

Analysis of Variance Procedure

Dependent Variable: PBREMV

Source	DF	Anova SS	Mean Square	F Value	Pr > F
SLRATIO	4	1486.21650	371.55412	11.58	0.0021
CONC	2	176.48168	88.24084	2.75	0.1232

Analysis of Variance Procedure

Waller-Duncan K-ratio T test for variable: PBREMV

NOTE: This test minimizes the Bayes risk under additive loss and certain other assumptions.

Kratio = 100 df = 8 MSE = 32.07382 F = 11.58434
Critical Value of T = 2.28590
Minimum Significant Difference = 10.57

Means with the same letter are not significantly different.

Waller Grouping	Mean	N	SLRATIO
A	24.467	3	0.005
A			
A	20.500	3	0.01
A			
A	14.400	3	0.05

Analysis of Variance Procedure

Waller Grouping	Mean	N	SLRATIO
B	1.130	3	0.2
B			
B	0.005	3	0.5

Analysis of Variance Procedure

Duncan's Multiple Range Test for variable: PBREMV

NOTE: This test controls the Type I comparisonwise error rate, not the experimentwise error rate

Alpha = 0.05 df = 8 MSE = 32.07382

Number of Means	2	3	4	5
Critical Range	10.66	11.11	11.36	11.51

Means with the same letter are not significantly different.

Duncan Grouping	Mean	N	SLRATIO
A	24.467	3	0.005
A			
A	20.500	3	0.01

Analysis of Variance Procedure

Duncan Grouping	Mean	N	SLRATIO
A			
A	14.400	3	0.05
B	1.130	3	0.2
B			
B	0.005	3	0.5

Analysis of Variance Procedure

Waller-Duncan K-ratio T test for variable: PBREMV

NOTE: This test minimizes the Bayes risk under additive loss and certain other assumptions.

ERROR: Failure in Bayes T computation. F value too small.

Comparison of Reaction Times to Reach Equilibrium Using Umatilla Soil, HCl, and an S:L Ratio of 0.05

OBS	SLRATIO	CONC	PB
1	24	0.01	0.115
2	24	0.05	24.149
3	24	0.1	22.562
4	30	0.01	0.100
5	30	0.05	19.900
6	30	0.1	23.200
7	48	0.01	0.100
8	48	0.05	15.900
9	48	0.1	23.900
10	60	0.01	2.100
11	60	0.05	21.200
12	60	0.1	23.700

Analysis of Variance Procedure

Class Level Information

Class	Levels	Values
SLRATIO	4	24 30 48 60
CONC	3	0.01 0.05 0.1

Number of observations in data set = 12

Analysis of Variance Procedure

Dependent Variable: PB

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	5	1229.70371	245.94074	53.10	0.0001
Error	6	27.79010	4.63168		

Corrected Total 11 1257.49381

R-Square	C.V.	Root MSE	PB Mean
0.977900	14.59685	2.15213	14.7438

Analysis of Variance Procedure

Dependent Variable: PB

Source	DF	Anova SS	Mean Square	F Value	Pr > F
SLRATIO	3	11.40730	3.80243	0.82	0.5281
CONC	2	1218.29641	609.14821	131.52	0.0001

Analysis of Variance Procedure

Waller-Duncan K-ratio T test for variable: PB

NOTE: This test minimizes the Bayes risk under additive loss and certain other assumptions.

ERROR: Failure in Bayes T computation. F value too small.

Analysis of Variance Procedure

Waller-Duncan K-ratio T test for variable: PB

NOTE: This test minimizes the Bayes risk under additive loss and certain other assumptions.

Kratio = 100 df = 6 MSE = 4.631683 F = 131.5177

Critical Value of T = 2.34292

Minimum Significant Difference = 3.5654

Means with the same letter are not significantly different.

Waller Grouping	Mean	N	CONC
A	23.341	4	0.1
A			
A	20.287	4	0.05
B	0.604	4	0.01

Analysis of Variance Procedure

Duncan's Multiple Range Test for variable: PB

NOTE: This test controls the Type I comparisonwise error rate, not the experimentwise error rate

Alpha = 0.05 df = 6 MSE = 4.631683

Number of Means	2	3
Critical Range	3.724	3.859

Means with the same letter are not significantly different.

Duncan Grouping	Mean	N	CONC
A	23.341	4	0.1
A			
A	20.287	4	0.05
B	0.604	4	0.01

Comparison of Reaction Times to Reach Equilibrium Using SE Fort Site 10 Soil, EDTA, and an S:L Ratio of 0.05.

OBS	SLRATIO	CONC	PB
1	24	0.01	1.127
2	24	0.05	1.771
3	24	0.1	4.518
4	30	0.01	1.300
5	30	0.05	1.800
6	30	0.1	0.800
7	48	0.01	1.600
8	48	0.05	2.400
9	48	0.1	0.800
10	60	0.01	1.700
11	60	0.05	3.000
12	60	0.1	0.900

Analysis of Variance Procedure Class Level Information

Class	Levels	Values
SLRATIO	4	24 30 48 60
CONC	3	0.01 0.05 0.1

Number of observations in data set = 12

Analysis of Variance Procedure

Dependent Variable: PB

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	5	3.57066617	0.71413323	0.47	0.7897
Error	6	9.17950650	1.52991775		
Corrected Total	11	12.75017267			

R-Square	C.V.	Root MSE	PB Mean
0.280048	68.34952	1.23690	1.80967

Analysis of Variance Procedure

Dependent Variable: PB

Source	DF	Anova SS	Mean Square	F Value	Pr > F
SLRATIO	3	2.23696400	0.74565467	0.49	0.7035
CONC	2	1.33370217	0.66685108	0.44	0.6657

Analysis of Variance Procedure

Waller-Duncan K-ratio T test for variable: PB

NOTE: This test minimizes the Bayes risk under additive loss and certain other assumptions.

ERROR: Failure in Bayes T computation. F value too small.

Analysis of Variance Procedure

Waller-Duncan K-ratio T test for variable: PB

NOTE: This test minimizes the Bayes risk under additive loss and certain other assumptions.

ERROR: Failure in Bayes T computation. F value too small.

Appendix C

Statistical Analysis for

Extractant Effectiveness

Batch Tests

Pb Removal Efficiency versus Extracting Agents

Note: Soils, extracting agents, and concentrations were assigned the following values.

1. SE Fort Site 10	A.	HNO ₃	a.	0.01 M
2. SE Fort Site 12	B.	HCl	b.	0.05 M
3. SE Fort Sites 5-8	C.	Fluorosilicic acid	c.	0.1 M
4. Umatilla	D.	Citric acid		
5. Fort Ord	E.	EDTA		
6. WES Spiked	F.	DTPA		
7. LAAP Site 1	G.	NTA		
8. LAAP Site 2	H.	NaOH		

OBS	SOIL	EXT	CONC	PB	CD	CR
1	1	A	a	55.1	0	0
2	1	A	b	99.0	0	0
3	1	A	c	35.4	0	0
4	1	B	a	99.0	0	0
5	1	B	b	36.3	0	0
6	1	B	c	58.5	0	0
7	1	C	a	3.8	0	0
8	1	C	b	37.7	0	0
9	1	C	c	8.3	0	0
10	1	D	a	29.5	0	0
11	1	D	b	17.1	0	0
12	1	D	c	99.0	0	0
13	1	E	a	14.5	0	0
14	1	E	b	9.6	0	0
15	1	E	c	42.4	0	0
16	1	F	a	17.0	0	0
17	1	F	b	35.5	0	0
18	1	F	c	99.0	0	0
19	1	G	a	14.0	0	0
20	1	G	b	11.7	0	0
21	1	G	c	10.7	0	0
22	1	H	a	0.1	0	0
23	1	H	b	0.0	0	0
24	1	H	c	3.0	0	0
25	2	A	a	99.0	0	0
26	2	A	b	99.0	0	0
27	2	A	c	99.0	0	0
28	2	B	a	66.9	0	0
29	2	B	b	99.0	0	0
30	2	B	c	99.0	0	0
31	2	C	a	91.6	0	0
32	2	C	b	99.0	0	0

OBS	SOIL	EXT	CONC	PB	CD	CR
33	2	C	c	99.0	0	0
34	2	D	a	29.0	0	0
35	2	D	b	64.7	0	0
36	2	D	c	99.0	0	0
37	2	E	a	30.9	0	0
38	2	E	b	56.3	0	0
39	2	E	c	83.3	0	0
40	2	F	a	78.9	0	0
41	2	F	b	84.1	0	0
42	2	F	c	16.9	0	0
43	2	G	a	14.0	0	0
44	2	G	b	99.0	0	0
45	2	G	c	99.0	0	0
46	2	H	a	0.1	0	0
47	2	H	b	14.0	0	0
48	2	H	c	52.4	0	0
49	3	A	a	97.4	0	0
50	3	A	b	99.0	0	0
51	3	A	c	99.0	0	0
52	3	B	a	62.8	0	0
53	3	B	b	99.0	0	0
54	3	B	c	99.0	0	0
55	3	C	a	50.9	0	0
56	3	C	b	99.0	0	0
57	3	C	c	99.0	0	0
58	3	D	a	14.7	0	0
59	3	D	b	43.2	0	0
60	3	D	c	68.6	0	0
61	3	E	a	49.4	0	0
62	3	E	b	51.7	0	0
63	3	E	c	85.7	0	0
64	3	F	a	78.9	0	0
65	3	F	b	99.0	0	0
66	3	F	c	99.0	0	0
67	3	G	a	99.0	0	0
68	3	G	b	99.0	0	0
69	3	G	c	99.0	0	0
70	3	H	a	0.4	0	0
71	3	H	b	41.2	0	0
72	3	H	c	89.1	0	0
73	4	A	a	8.6	0	0
74	4	A	b	99.0	0	0
75	4	A	c	99.0	0	0
76	4	B	a	1.5	0	0
77	4	B	b	99.0	0	0
78	4	B	c	99.0	0	0
79	4	C	a	26.7	0	0

OBS	SOIL	EXT	CONC	PB	CD	CR
80	4	C	b	99.0	0	0
81	4	C	c	99.0	0	0
82	4	D	a	46.2	0	0
83	4	D	b	46.6	0	0
84	4	D	c	99.0	0	0
85	4	E	a	13.6	0	0
86	4	E	b	23.9	0	0
87	4	E	c	35.9	0	0
88	4	F	a	52.9	0	0
89	4	F	b	74.0	0	0
90	4	F	c	93.9	0	0
91	4	G	a	99.0	0.0	0.0
92	4	G	b	23.9	0.0	0.0
93	4	G	c	99.0	0.0	0.0
94	4	H	a	0.3	0.0	0.0
95	4	H	b	14.1	0.0	0.0
96	4	H	c	33.8	0.0	0.0
97	5	A	a	46.4	0.0	0.0
98	5	A	b	99.0	0.0	0.0
99	5	A	c	27.4	0.0	0.0
100	5	B	a	85.9	0.0	0.0
101	5	B	b	78.1	0.0	0.0
102	5	B	c	49.5	0.0	0.0
103	5	C	a	57.3	0.0	0.0
104	5	C	b	89.9	0.0	0.0
105	5	C	c	37.7	0.0	0.0
106	5	D	a	16.1	0.0	0.0
107	5	D	b	32.4	0.0	0.0
108	5	D	c	37.6	0.0	0.0
109	5	E	a	17.1	0.0	0.0
110	5	E	b	26.5	0.0	0.0
111	5	E	c	21.0	0.0	0.0
112	5	F	a	32.3	0.0	0.0
113	5	F	b	26.9	0.0	0.0
114	5	F	c	18.9	0.0	0.0
115	5	G	a	51.4	0.0	0.0
116	5	G	b	85.6	0.0	0.0
117	5	G	c	26.7	0.0	0.0
118	5	H	a	1.8	0.0	0.0
119	5	H	b	9.3	0.0	0.0
120	5	H	c	14.7	0.0	0.0
121	6	A	a	0.1	91.1	0.0
122	6	A	b	7.9	99.0	0.0
123	6	A	c	36.2	99.0	0.0
124	6	B	a	0.3	82.9	0.0
125	6	B	b	28.2	99.0	0.0
126	6	B	c	47.4	99.0	0.4

OBS	SOIL	EXT	CONC	PB	CD	CR
127	6	C	a	14.7	99.0	20.6
128	6	C	b	99.0	99.0	99.0
129	6	C	c	99.0	99.0	99.0
130	6	D	a	45.0	88.5	4.7
131	6	D	b	99.0	99.0	33.7
132	6	D	c	99.0	99.0	62.6
133	6	E	a	80.5	99.0	0.3
134	6	E	b	95.9	97.0	0.6
135	6	E	c	99.0	99.0	0.0
136	6	F	a	99.0	99.0	0.0
137	6	F	b	99.0	99.0	0.0
138	6	F	c	99.0	99.0	2.6
139	6	G	a	83.4	99.0	0.9
140	6	G	b	99.0	99.0	2.6
141	6	G	c	48.3	90.6	3.8
142	6	H	a	0.0	0.0	0.0
143	6	H	b	3.3	0.0	0.0
144	6	H	c	11.8	0.0	0.8

Analysis of Variance Procedure
Class Level Information

Class	Levels	Values
SOIL	6	1 2 3 4 5 6
EXT	8	A B C D E F G H
CONC	3	a b c

Number of observations in data set = 144

Analysis of Variance Procedure

Dependent Variable: PB

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	14	87570.9571	6255.0684	7.53	0.0001
Error	129	107158.9923	830.6899		
Corrected Total	143	194729.9494			

R-Square	C.V.	Root MSE	PB Mean
0.449705	51.22149	28.8217	56.2687

Source	DF	Anova SS	Mean Square	F Value	Pr > F
SOIL	5	30223.7373	6044.7475	7.28	0.0001
EXT	7	40455.5544	5779.3649	6.96	0.0001
CONC	2	16891.6654	8445.8327	10.17	0.0001

Analysis of Variance Procedure

Waller-Duncan K-ratio T test for variable: PB

NOTE: This test minimizes the Bayes risk under additive loss and certain other assumptions.

Kratio = 100 df = 129 MSE = 830.6899 F = 7.27678

Critical Value of T = 1.88398

Minimum Significant Difference = 15.675

Means with the same letter are not significantly different.

Waller Grouping	Mean	N	SOIL
A	75.958	24	3
A			
B A	69.713	24	2
B			
B	58.083	24	6
B			
B	57.788	24	4
C	41.229	24	5
C			
C	34.842	24	1

Analysis of Variance Procedure

Duncan's Multiple Range Test for variable: PB

NOTE: This test controls the Type I comparisonwise error rate, not the experimentwise error rate

Alpha = 0.05 df = 129 MSE = 830.6899

Number of Means	2	3	4	5	6
Critical Range	16.46	17.33	17.90	18.32	18.65

Means with the same letter are not significantly different.

Duncan Grouping	Mean	N	SOIL
A	75.958	24	3
A			
B A	69.713	24	2
B			
B C	58.083	24	6
B C			
B C	57.788	24	4
C			
D C	41.229	24	5
D			
D	34.842	24	1

Analysis of Variance Procedure

Waller-Duncan K-ratio T test for variable: PB

NOTE: This test minimizes the Bayes risk under additive loss and certain other assumptions.

Kratio = 100 df = 129 MSE = 830.6899 F = 6.957308
Critical Value of T = 1.89042

Minimum Significant Difference = 18.162

Means with the same letter are not significantly different.

Waller Grouping	Mean	N	EXT
A	67.256	18	C
A			
A	67.133	18	B
A			
A	66.972	18	A
A			
A	66.900	18	F
A			
B A	64.539	18	G
B A			
B A	54.761	18	D
B			
B	46.511	18	E
C	16.078	18	H

Analysis of Variance Procedure

Duncan's Multiple Range Test for variable: PB

NOTE: This test controls the Type I comparisonwise error rate, not the experimentwise error rate

Alpha = 0.05 df = 129 MSE = 830.6899

Number of Means	2	3	4	5	6	7	8
Critical Range	19.01	20.01	20.67	21.16	21.54	21.84	22.10

Means with the same letter are not significantly different.

Duncan Grouping	Mean	N	EXT
A	67.256	18	C
A			
A	67.133	18	B
A			
A	66.972	18	A
A			
A	66.900	18	F
A			
A	64.539	18	G
A			
A	54.761	18	D
A			
A	46.511	18	E
B	16.078	18	H

Analysis of Variance Procedure

Waller-Duncan K-ratio T test for variable: PB

NOTE: This test minimizes the Bayes risk under additive loss and certain other assumptions.

Kratio = 100 df = 129 MSE = 830.6899 F = 10.16725

Critical Value of T = 1.84290

Minimum Significant Difference = 10.842

Means with the same letter are not significantly different.

Waller Grouping	Mean	N	CONC
A	66.127	48	c
A			
A	61.492	48	b
B	41.188	48	a

Analysis of Variance Procedure

Duncan's Multiple Range Test for variable: PB

NOTE: This test controls the Type I comparisonwise error rate, not the experimentwise error rate

Alpha = 0.05 df = 129 MSE = 830.6899

Number of Means	2	3
Critical Range	11.64	12.25

Means with the same letter are not significantly different.

Duncan Grouping	Mean	N	CONC
A	66.127	48	c
A			
A	61.492	48	b
B	41.188	48	a

Cd Removal Efficiency versus Extracting Agents

OBS	SOIL	EXT	CONC	PB	CD	CR
1	6	A	a	0.1	91.1	0.0
2	6	A	b	7.9	99.0	0.0
3	6	A	c	36.2	99.0	0.0
4	6	B	a	0.3	82.9	0.0
5	6	B	b	28.2	99.0	0.0
6	6	B	c	47.4	99.0	0.4
7	6	C	a	14.7	99.0	20.6
8	6	C	b	99.0	99.0	99.0
9	6	C	c	99.0	99.0	99.0
10	6	D	a	45.0	88.5	4.7
11	6	D	b	99.0	99.0	33.7
12	6	D	c	99.0	99.0	62.6
13	6	E	a	80.5	99.0	0.3
14	6	E	b	95.9	97.0	0.6
15	6	E	c	99.0	99.0	0.0

OBS	SOIL	EXT	CONC	PB	CD	CR
16	6	F	a	99.0	99.0	0.0
17	6	F	b	99.0	99.0	0.0
18	6	F	c	99.0	99.0	2.6
19	6	G	a	83.4	99.0	0.9
20	6	G	b	99.0	99.0	2.6
21	6	G	c	48.3	90.6	3.8
22	6	H	a	0.0	0.0	0.0
23	6	H	b	3.3	0.0	0.0
24	6	H	c	11.8	0.0	0.8
25	8	A	a	0.0	16.2	0.0
26	8	A	b	0.0	99.0	24.9
27	8	A	c	0.0	99.0	58.3
28	8	B	a	0.0	32.4	0.0
29	8	B	b	0.0	99.0	22.4
30	8	B	c	0.0	99.0	54.5
31	8	C	a	0.0	86.5	13.0
32	8	C	b	0.0	99.0	57.8
33	8	C	c	0.0	99.0	99.0
34	8	D	a	0.0	64.9	25.8
35	8	D	b	0.0	99.0	59.1
36	8	D	c	0.0	99.0	74.1
37	8	E	a	0.0	75.5	0.0
38	8	E	b	0.0	32.4	0.1
39	8	E	c	0.0	99.0	0.0
40	8	F	a	0.0	86.5	0.0
41	8	F	b	0.0	5.9	0.0
42	8	F	c	0.0	97.3	0.7
43	8	G	a	0.0	91.9	2.4
44	8	G	b	0.0	99.0	10.8
45	8	G	c	0.0	99.0	16.5
46	8	H	a	0	0.6	0.3
47	8	H	b	0	0.0	0.0
48	8	H	c	0	0.0	0.0

Analysis of Variance Procedure
Class Level Information

Class	Levels	Values
SOIL	2	6 8
EXT	8	A B C D E F G H
CONC	3	a b c

Number of observations in data set = 48

Analysis of Variance Procedure

Dependent Variable: CD

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	10	47249.4129	4724.9413	10.97	0.0001
Error	37	15938.6438	430.7742		
Corrected Total	47	63188.0567			

R-Square	C.V.	Root MSE	CD Mean
0.747759	26.82982	20.7551	77.3583

Source	DF	Anova SS	Mean Square	F Value	Pr > F
SOIL	1	2625.5208	2625.5208	6.09	0.0183
EXT	7	42447.0867	6063.8695	14.08	0.0001
CONC	2	2176.8054	1088.4027	2.53	0.0936

Analysis of Variance Procedure

Waller-Duncan K-ratio T test for variable: CD

NOTE: This test minimizes the Bayes risk under additive loss and certain other assumptions.

Analysis of Variance Procedure

Waller-Duncan K-ratio T test for variable: CD

NOTE: This test minimizes the Bayes risk under additive loss and certain other assumptions.

Kratio = 100 df = 37 MSE = 430.7742 F = 14.07668

Critical Value of T = 1.87271

Minimum Significant Difference = 22.441

Means with the same letter are not significantly different.

Waller Grouping	Mean	N	EXT
A	96.92	6	C
A			
A	96.42	6	G
A			
A	91.57	6	D
A			
A	85.22	6	B
A			
A	83.88	6	A
A			
A	83.65	6	E
A			
A	81.12	6	F
B	0.10	6	H

Analysis of Variance Procedure

Duncan's Multiple Range Test for variable: CD

NOTE: This test controls the Type I comparisonwise error rate, not the experimentwise error rate

Alpha = 0.05 df = 37 MSE = 430.7742

Number of Means	2	3	4	5	6	7	8
Critical Range	24.28	25.53	26.34	26.92	27.37	27.72	28.01

Means with the same letter are not significantly different.

Duncan Grouping	Mean	N	EXT
A	96.92	6	C
A			
A	96.42	6	G
A			
A	91.57	6	D
A			
A	85.22	6	B
A			
A	83.88	6	A
A			
A	83.65	6	E
A			
A	81.12	6	F
B	0.10	6	H

Analysis of Variance Procedure

Waller-Duncan K-ratio T test for variable: CD

NOTE: This test minimizes the Bayes risk under additive loss and certain other assumptions.

Kratio = 100 df = 37 MSE = 430.7742 F = 2.52662

Critical Value of T = 2.22589

Minimum Significant Difference = 16.334

Means with the same letter are not significantly different.

Waller Grouping	Mean	N	CONC
A	85.994	16	c
A			
B A	76.519	16	b
B			
B	69.563	16	a

Analysis of Variance Procedure

Duncan's Multiple Range Test for variable: CD

NOTE: This test controls the Type I comparisonwise error rate, not the experimentwise error rate

Alpha = 0.05 df = 37 MSE = 430.7742

Number of Means 2 3

Critical Range 14.87 15.63

Means with the same letter are not significantly different.

Duncan Grouping	Mean	N	CONC
A	85.994	16	c
A			
B A	76.519	16	b
B			
B	69.563	16	a

Cr Removal Efficiency versus Extracting Agents

OBS	SOIL	EXT	CONC	PB	CD	CR
1	6	A	a	0.1	91.1	0.0
2	6	A	b	7.9	99.0	0.0
3	6	A	c	36.2	99.0	0.0
4	6	B	a	0.3	82.9	0.0
5	6	B	b	28.2	99.0	0.0
6	6	B	c	47.4	99.0	0.4
7	6	C	a	14.7	99.0	20.6
8	6	C	b	99.0	99.0	99.0
9	6	C	c	99.0	99.0	99.0
10	6	D	a	45.0	88.5	4.7
11	6	D	b	99.0	99.0	33.7
12	6	D	c	99.0	99.0	62.6
13	6	E	a	80.5	99.0	0.3
14	6	E	b	95.9	97.0	0.6
15	6	E	c	99.0	99.0	0.0
16	6	F	a	99.0	99.0	0.0
17	6	F	b	99.0	99.0	0.0
18	6	F	c	99.0	99.0	2.6
19	6	G	a	83.4	99.0	0.9
20	6	G	b	99.0	99.0	2.6
21	6	G	c	48.3	90.6	3.8
22	6	H	a	0.0	0.0	0.0
23	6	H	b	3.3	0.0	0.0
24	6	H	c	11.8	0.0	0.8
25	7	A	a	0.0	0.0	20.3
26	7	A	b	0.0	0.0	28.6
27	7	A	c	0.0	0.0	41.2
28	7	B	a	0.0	0.0	15.9
29	7	B	b	0.0	0.0	23.5
30	7	B	c	0.0	0.0	32.9
31	7	C	a	0.0	0.0	9.8
32	7	C	b	0.0	0.0	34.7
33	7	C	c	0.0	0.0	50.6
34	7	D	a	0.0	0.0	26.8
35	7	D	b	0.0	0.0	28.6
36	7	D	c	0.0	0.0	29.3
37	7	E	a	0.0	0.0	14.5
38	7	E	b	0.0	0.0	0.0
39	7	E	c	0.0	0.0	0.0
40	7	F	a	0.0	0.0	0.0
41	7	F	b	0.0	0.0	1.5
42	7	F	c	0.0	0.0	6.1
43	7	G	a	0.0	0.0	26.8
44	7	G	b	0.0	0.0	28.6
45	7	G	c	0.0	0.0	28.2

OBS	SOIL	EXT	CONC	PB	CD	CR
46	7	H	a	0	0.0	16.6
47	7	H	b	0	0.0	16.3
48	7	H	c	0	0.0	18.1
49	8	A	a	0	16.2	0.0
50	8	A	b	0	99.0	24.9
51	8	A	c	0	99.0	58.3
52	8	B	a	0	32.4	0.0
53	8	B	b	0	99.0	22.4
54	8	B	c	0	99.0	54.5
55	8	C	a	0	86.5	13.0
56	8	C	b	0	99.0	57.8
57	8	C	c	0	99.0	99.0
58	8	D	a	0	64.9	25.8
59	8	D	b	0	99.0	59.1
60	8	D	c	0	99.0	74.1
61	8	E	a	0	75.5	0.0
62	8	E	b	0	32.4	0.1
63	8	E	c	0	99.0	0.0
64	8	F	a	0	86.5	0.0
65	8	F	b	0	5.9	0.0
66	8	F	c	0	97.3	0.7
67	8	G	a	0	91.9	2.4
68	8	G	b	0	99.0	10.8
69	8	G	c	0	99.0	16.5
70	8	H	a	0	0.6	0.3
71	8	H	b	0	0.0	0.0
72	8	H	c	0	0.0	0.0

Analysis of Variance Procedure
Class Level Information

Class	Levels	Values
SOIL	3	6 7 8
EXT	8	A B C D E F G H
CONC	3	a b c

Number of observations in data set = 72

Analysis of Variance Procedure

Dependent Variable: CR

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	11	27356.3733	2486.9430	8.37	0.0001
Error	60	17822.9461	297.0491		
Corrected Total	71	45179.3194			

R-Square	C.V.	Root MSE	CR Mean
0.605507	91.90698	17.2351	18.7528

Source	DF	Anova SS	Mean Square	F Value	Pr > F
SOIL	2	886.1603	443.0801	1.49	0.2332
EXT	7	21637.9128	3091.1304	10.41	0.0001
CONC	2	4832.3003	2416.1501	8.13	0.0007

Analysis of Variance Procedure

Waller-Duncan K-ratio T test for variable: CR

NOTE: This test minimizes the Bayes risk under additive loss and certain other assumptions.

ERROR: Failure in Bayes T computation. F value too small.

Analysis of Variance Procedure

Waller-Duncan K-ratio T test for variable: CR

NOTE: This test minimizes the Bayes risk under additive loss and certain other assumptions.

Kratio = 100 df = 60 MSE = 297.0491 F = 10.40613

Critical Value of T = 1.86485

Minimum Significant Difference = 15.151

Means with the same letter are not significantly different.

Waller Grouping	Mean	N	EXT
A	53.722	9	C
B	38.300	9	D

Waller Grouping	Mean	N	EXT
C	19.256	9	A
C			
D C	16.622	9	B
D C			
D C E	13.400	9	G
D C E			
D C E	5.789	9	H
D E			
D E	1.722	9	E
E			
E	1.211	9	F

Analysis of Variance Procedure

Duncan's Multiple Range Test for variable: CR

NOTE: This test controls the Type I comparisonwise error rate, not the experimentwise error rate

Alpha = 0.05 df = 60 MSE = 297.0491

Number of Means	2	3	4	5	6	7	8
Critical Range	16.25	17.10	17.65	18.06	18.37	18.62	18.83

Means with the same letter are not significantly different.

Duncan Grouping	Mean	N	EXT
A	53.722	9	C
A			
A	38.300	9	D
B	19.256	9	A
B			
B	16.622	9	B
B			
B	13.400	9	G
B			
B	5.789	9	H
B			
B	1.722	9	E
B			
B	1.211	9	F

Analysis of Variance Procedure

Waller-Duncan K-ratio T test for variable: CR

NOTE: This test minimizes the Bayes risk under additive loss and certain other assumptions.

Kratio = 100 df = 60 MSE = 297.0491 F = 8.133841

Critical Value of T = 1.90320

Minimum Significant Difference = 9.4691

Means with the same letter are not significantly different.

Waller Grouping	Mean	N	CONC
A	28.279	24	c
A			
A	19.700	24	b
B	8.279	24	a

Analysis of Variance Procedure

Duncan's Multiple Range Test for variable: CR

NOTE: This test controls the Type I comparisonwise error rate, not the experimentwise error rate

Alpha = 0.05 df = 60 MSE = 297.0491

Number of Means	2	3
Critical Range	9.95	10.47

Means with the same letter are not significantly different.

Duncan Grouping	Mean	N	CONC
A	28.279	24	c
A			
A	19.700	24	b
B	8.279	24	a

Appendix D

Data for Equilibrium Test

CONTROL PANEL		
Soil Type	: WES Spk.	Lo : 85.0
Extractant	: .05 M EDTA	k : 0.7
Contaminant : Pb		
Curve Type : 1st Order		

Time, Hrs	Fitted Curve, % Removal	Raw Data, % Removal
0	0	
0.5	47.031894667	67.493413
1	68.040270323	73.90128
2	81.61608905	78.369928
3	84.324821	81.236606
5	84.97312064	81.278763
7	84.998929913	81.426313
10	84.99999915	82.901809
12	84.999999662	82.227297
14	84.999999987	81.658177
16	84.999999999	82.121904
18	85	77.948358
20	85	84.545934
22	85	84.524855
24	85	85.578781
26	85	82.18514
28	85	87.665554
30	85	86.358686

Soil Type : WES Spk.

Lo : 85.0

Extractant : .05 M EDTA

 $\mathbf{k} : \mathbf{k} \quad 0.7$

Contaminant : Pb

Curve Type : 1st Order

Time, Hrs	Fitted Curve, % Removal	Raw Data, % Removal
0	0	
0.5	47.031894667	67.493413
1	68.040270323	73.90128
2	81.61608905	78.369928
3	84.324821	81.236606
5	84.97312064	81.278763
7	84.998929913	81.426313
10	84.9999915	82.901809
12	84.999999662	82.227297
14	84.999999987	81.658177
16	84.999999999	82.121904
18	85	77.948358
20	85	84.545934
22	85	84.524855
24	85	85.578781
26	85	82.18514
28	85	87.665554
30	85	86.358686

CONTROL PANEL		
Soil Type : WES Spk.	Lo :	85.0
Extractant : .05 M EDTA	k :	0.4
Contaminant : Cd		
Curve Type : 1st Order		

Time, Hrs	Fitted Curve, % Removal	Raw Data, % Removal
0	0	
0.5	31.368625719	58.108108
1	15.160890503	64.264264
2	71.528407864	71.921922
3	79.636862572	77.777778
5	84.15	78.228228
7	84.865284079	77.327327
10	84.9915	80.630636
12	84.998652841	80.480481
14	84.99978649	80.630631
16	84.999966161	81.681682
18	84.999994637	75.075
20	84.99999915	83.633634
22	84.999999865	84.384384
24	84.999999979	83.483484
26	84.999999997	80.33033
28	84.999999999	85.885886
30	85	86.036036

Soil Type : WES Spk.

Lo : 85.0

Extractant : .05 M EDTA

k : 0.4

Contaminant : Cd

Curve Type : 1st Order

Time, Hrs	Fitted Curve, % Removal	Raw Data, % Removal
0	0	
0.5	31.368625719	58.108108
1	15.160890503	64.264264
2	71.528407864	71.921922
3	79.636862572	77.777778
5	84.15	78.228228
7	84.865284079	77.327327
10	84.9915	80.630636
12	84.998652841	80.480481
14	84.99978649	80.630631
16	84.999966161	81.681682
18	84.999994637	75.075
20	84.99999915	83.633634
22	84.999999865	84.384384
24	84.999999979	83.483484
26	84.999999997	80.33033
28	84.999999999	85.885886
30	85	86.036036

CONTROL PANEL Soil Type : WES Spk. Extractant : .05 M EDTA Contaminant : Cr Curve Type : 1st Order			Lo : 1.2 k : 2e+09
Time, Hrs	Fitted Curve, % Removal	Raw Data, % Removal	
0	0		
0.5	1.206695	1.5570261	
1	1.206695	1.79058	
2	1.206695	0.9342157	
3	1.206695	1.0899183	
5	1.206695	1.0899183	
7	1.206695	1.012067	
10	1.206695	1.0899183	
12	1.206695	1.0899183	
14	1.206695	1.0899183	
16	1.206695	1.1677696	
18	1.206695	1.6348774	
20	1.206695	1.3234722	
22	1.206695	1.2456209	
24	1.206695	1.2456209	
26	1.206695	1.1677696	
28	1.206695	1.1677696	
30	1.206695	1.1677696	

CONTROL PANEL Soil Type : WES Spk. Extractant : .05 M EDTA Contaminant : Pb Curve Type : 1st Order			Lo : 88.0 k : 0.7
Time, Hrs	Fitted Curve, % Removal	Raw Data, % Removal	
0	0		
0.5	48.691843891	68.568665	
1	70.441691628	77.775629	
2	84.496656899	80	
3	87.300991153	85.009671	
5	87.972171957	85.24178	
7	87.998892146	86.576402	
10	87.9999912	87.079304	
12	87.99999965	87.079304	
14	87.999999986	85.222437	
16	87.999999999	85.203095	
18	88	88.626693	
20	88	89.071567	
22	88	88.433269	
24	88	89.555126	
26	88	91.257253	
28	88	90.947776	
30	88	88.68472	

CONTROL PANEL		
Soil Type	: WES Spk.	Lo : 87.0
Extractant	: .05 M EDTA	k : 0.5
Contaminant : Cd		
Curve Type : 1st Order		

Time, Hrs	Fitted Curve, % Removal	Raw Data, % Removal
0	0	
0.5	38.076304708	58.287359
1	59.488184357	69.656992
2	78.3	74.118494
3	84.248818436	81.602303
5	86.724881844	82.465819
7	86.972488184	83.761094
10	86.99913	84.76853
12	86.999913	84.192852
14	86.9999913	83.473255
16	86.99999913	83.905013
18	86.999999913	86.639482
20	86.999999991	87.502998
22	86.999999999	86.927321
24	87	88.510434
26	87	90.381386
28	87	89.373951
30	87	87.646918

Soil Type : WES Spk.

Lo : 87.0

Extractant : .05 M EDTA

k : 0.5

Contaminant : Cd

Curve Type : 1st Order

Time, Hrs	Fitted Curve, % Removal	Raw Data, % Removal
0	0	
0.5	38.076304708	58.287359
1	59.488184357	69.656992
2	78.3	74.118494
3	84.248818436	81.602303
5	86.724881844	82.465819
7	86.972488184	83.761094
10	86.99913	84.76853
12	86.999913	84.192852
14	86.9999913	83.473255
16	86.99999913	83.905013
18	86.999999913	86.639482
20	86.999999991	87.502998
22	86.999999999	86.927321
24	87	88.510434
26	87	90.381386
28	87	89.373951
30	87	87.646918

CONTROL PANEL		
Soil Type	: WES Spk.	Lo : 1.0
Extractant	: .05 M DTPA	k : 1.4
Contaminant : Cr		
Curve Type : 1st Order		
Time, Hrs	Fitted Curve, % Removal	Raw Data, % Removal
0	0	
0.5	0.8247467372	0.8352668
1	0.9947215635	0.974478
2	1.0369718378	0.974478
3	1.0387663959	1.0440835
5	1.0388458564	1.0440835
7	1.0388459997	1.0440835
10	1.038846	1.0440835
12	1.038846	1.0440835
14	1.038846	0.974478
16	1.038846	1.0440835
18	1.038846	1.0440835
20	1.038846	1.0440835
22	1.038846	1.1136891
24	1.038846	1.0440835
26	1.038846	1.0440835
28	1.038846	1.0440835
30	1.038846	1.0440835

Soil Type : WES Spk.

Lo : 1.0

Extractant : .05 M DTPA

k : 1.4

Contaminant : Cr

Curve Type : 1st Order

Time, Hrs	Fitted Curve, % Removal	Raw Data, % Removal
0	0	
0.5	0.8247467372	0.8352668
1	0.9947215635	0.974478
2	1.0369718378	0.974478
3	1.0387663959	1.0440835
5	1.0388458564	1.0440835
7	1.0388459997	1.0440835
10	1.038846	1.0440835
12	1.038846	1.0440835
14	1.038846	0.974478
16	1.038846	1.0440835
18	1.038846	1.0440835
20	1.038846	1.0440835
22	1.038846	1.1136891
24	1.038846	1.0440835
26	1.038846	1.0440835
28	1.038846	1.0440835
30	1.038846	1.0440835

CONTROL PANEL Soil Type : Umatilla Extractant : .05 M HNO₃ Contaminant : Pb Curve Type : 1st Order			Lo : 92.0 k : 0.2
Time, Hrs	Fitted Curve, % Removal	Raw Data, % Removal	
0	0		
0.5	14.591646969	60.92049	
1	26.868987837	65.907466	
2	45.890774506	70.951115	
3	59.357168191	73.727956	
5	75.639829428	79.443552	
7	83.800491369	81.564638	
10	89.090704553	86.664958	
12	90.541898263	87.393575	
14	91.269218024	87.757883	
16	91.633741403	91.206671	
18	91.816435867	86.9645	
20	91.908	95.392171	
22	91.953890775	92.356267	
24	91.976890645	93.133458	
26	91.988417886	93.101075	
28	91.994195192	91.813852	
30	91.997090705	90.761405	

CONTROL PANEL Soil Type : Umatilla Extractant : .05 M Citric Contaminant : Pb Curve Type : 1st Order			Lo : 53.5 k : 0.5
Time, Hrs	Fitted Curve, % Removal	Raw Data, % Removal	
0	0		
0.5	24.776099351	28.44844	
1	38.076772733	36.31031	
2	49.050180605	46.52791	
3	52.2126251	51.41911	
5	53.386670201	52.715	
7	53.484179843	58.524	
10	53.492800597	57.01	
12	53.492994442	61.532	
14	53.493010542	64.938	
16	53.493011879	62.573	
18	53.49301199	66.906	
20	53.493011999	66.934	
22	53.493012	66.395	
24	53.493012	38.438	
26	53.493012	25.383	
28	53.493012	39.224	
30	53.493012	37.36	

CONTROL PANEL		
Soil Type : Umatilla	Lo :	35.0
Extractant : .05 M EDTA	k :	0.1
Contaminant : Pb		
Curve Type : 1st Order		

Time, Hrs	Fitted Curve, % Removal	Raw Data, % Removal
0	0	
0.5	3.8062171653	10.679
1	7.1985117847	11.662
2	12.916492943	14.785
3	17.458446823	17.946
5	23.932028189	19.566
7	28.016581898	22.11
10	31.5	25.465
12	32.791649294	26.371
14	33.606624903	27.585
16	34.120839749	30.669
18	34.445287383	32.424
20	34.65	33.773
22	34.779164929	34.949
24	34.86066249	35.72
26	34.912083975	40.077
28	34.944528738	40.655
30	34.965	41.831

Soil Type : Umatilla
Extractant : .05 M EDTA
Contaminant : Pb
Curve Type : 1st Order

Lo : 35.0
k : 0.1

Time, Hrs	Fitted Curve, % Removal	Raw Data, % Removal
0	0	
0.5	3.8062171653	10.679
1	7.1985117847	11.662
2	12.916492943	14.785
3	17.458446823	17.946
5	23.932028189	19.566
7	28.016581898	22.11
10	31.5	25.465
12	32.791649294	26.371
14	33.606624903	27.585
16	34.120839749	30.669
18	34.445287383	32.424
20	34.65	33.773
22	34.779164929	34.949
24	34.86066249	35.72
26	34.912083975	40.077
28	34.944528738	40.655
30	34.965	41.831

CONTROL PANEL		
Soil Type : Umatilla	Lo :	61.3
Extractant : .05 M DTPA	k :	0.1
Contaminant : Pb		
Curve Type : 1st Order		
Time, Hrs	Fitted Curve, % Removal	Raw Data, % Removal
0	0	
0.5	5.4917592319	16.785
1	10.491879479	21.364
2	19.189314909	27.892
3	26.399213116	33.647
5	37.330548774	36.231
7	44.842436183	42.094
10	51.944039701	45.157
12	54.884658099	49.025
14	56.905417044	49.504
16	58.294059215	47.617
18	59.248318051	56.961
20	59.904073684	59.467
22	60.354701369	63.134
24	60.664367501	63.582
26	60.877166485	62.438
28	61.023399485	67.79
30	61.123889111	71.859

Soil Type : Umatilla
Extractant : .05 M DTPA
Contaminant : Pb
Curve Type : 1st Order

Lo : 61.3
k : 0.1

Time, Hrs	Fitted Curve, % Removal	Raw Data, % Removal
0	0	
0.5	5.4917592319	16.785
1	10.491879479	21.364
2	19.189314909	27.892
3	26.399213116	33.647
5	37.330548774	36.231
7	44.842436183	42.094
10	51.944039701	45.157
12	54.884658099	49.025
14	56.905417044	49.504
16	58.294059215	47.617
18	59.248318051	56.961
20	59.904073684	59.467
22	60.354701369	63.134
24	60.664367501	63.582
26	60.877166485	62.438
28	61.023399485	67.79
30	61.123889111	71.859

CONTROL PANEL		
Soil Type : WES Spk.	Lo :	61.6
Extractant : .05 M Citric	k :	14.4
Contaminant : Pb		
Curve Type : 1st Order		
Time, Hrs	Fitted Curve, % Removal	Raw Data, % Removal
0	0	
0.5	61.646580117	61.857
1	61.646584	60.706
2	61.646584	60.023
3	61.646584	56.162
5	61.646584	57.229
7	61.646584	57.357
10	61.646584	58.743
12	61.646584	59.874
14	61.646584	59.319
16	61.646584	59.532
18	61.646584	61.623
20	61.646584	60.919
22	61.646584	61.665
24	61.646584	60.812
26	61.646584	62.519
28	61.646584	63.287
30	61.646584	64.609

CONTROL PANEL		
Soil Type : WES Spk.	Lo :	86.5
Extractant : .05 M Citric	k :	3.5
Contaminant : Cd		
Curve Type : 1st Order		
Time, Hrs	Fitted Curve, % Removal	Raw Data, % Removal
0	0	
0.5	85.012303436	85.056
1	86.474051185	85.191
2	86.499617439	86.275
3	86.499624998	82.618
5	86.499625	87.494
7	86.499625	86.004
10	86.499625	87.358
12	86.499625	86.546
14	86.499625	86.41
16	86.499625	84.65
18	86.499625	87.494
20	86.499625	86.41
22	86.499625	86.952
24	86.499625	86.817
26	86.499625	88.036
28	86.499625	86.546
30	86.499625	89.119

CONTROL PANEL		
Soil Type : WES Spk.	Lo :	1.1
Extractant : .05 M Citric	k :	2349.8
Contaminant : Cr		
Curve Type : 1st Order		

Time, Hrs	Fitted Curve, % Removal	Raw Data, % Removal
0	0	
0.5	1.0868823	1.402
1	1.0868823	1.612
2	1.0868823	0.841
3	1.0868823	0.981
5	1.0868823	0.981
7	1.0868823	0.911
10	1.0868823	0.981
12	1.0868823	0.981
14	1.0868823	0.981
16	1.0868823	1.051
18	1.0868823	1.472
20	1.0868823	1.192
22	1.0868823	1.122
24	1.0868823	1.122
26	1.0868823	1.051
28	1.0868823	1.051
30	1.0868823	1.051

Soil Type : WES Spk.
Extractant : .05 M Citric
Contaminant : Cr
Curve Type : 1st Order

Lo : **1.1**
k : **2349.8**

Time, Hrs	Fitted Curve, % Removal	Raw Data, % Removal
0	0	
0.5	1.0868823	1.402
1	1.0868823	1.612
2	1.0868823	0.841
3	1.0868823	0.981
5	1.0868823	0.981
7	1.0868823	0.911
10	1.0868823	0.981
12	1.0868823	0.981
14	1.0868823	0.981
16	1.0868823	1.051
18	1.0868823	1.472
20	1.0868823	1.192
22	1.0868823	1.122
24	1.0868823	1.122
26	1.0868823	1.051
28	1.0868823	1.051
30	1.0868823	1.051

CONTROL PANEL		
Soil Type	: LAAP Site 2	Lo : 94.5
Extractant	: .05 M HNO ₃	k : 2.2
Contaminant : Cd		
Curve Type : 1st Order		
Time, Hrs	Fitted Curve, % Removal	Raw Data, % Removal
0	0	
0.5	86.731873981	86.835
1	93.878423875	93.267
2	94.515807923	93.267
3	94.520135418	96.483
5	94.520164999	96.483
7	94.520165	83.619
10	94.520165	99.699
12	94.520165	96.483
14	94.520165	86.483
16	94.520165	96.483
18	94.520165	93.267
20	94.520165	96.483
22	94.520165	96.483
24	94.520165	93.267
26	94.520165	93.267
28	94.520165	93.267
30	94.520165	93.267

Soil Type : LAAP Site 2
Extractant : .05 M HNO₃
Contaminant : Cd
Curve Type : 1st Order

Lo : **94.5**
k : **2.2**

Time, Hrs	Fitted Curve, % Removal	Raw Data, % Removal
0	0	
0.5	86.731873981	86.835
1	93.878423875	93.267
2	94.515807923	93.267
3	94.520135418	96.483
5	94.520164999	96.483
7	94.520165	83.619
10	94.520165	99.699
12	94.520165	96.483
14	94.520165	86.483
16	94.520165	96.483
18	94.520165	93.267
20	94.520165	96.483
22	94.520165	96.483
24	94.520165	93.267
26	94.520165	93.267
28	94.520165	93.267
30	94.520165	93.267

CONTROL PANEL Soil Type : LAAP Site 2 Extractant : .05 M HNO₃ Contaminant : Cr Curve Type : 1st Order			Lo : 85.9 k : 2.9
Time, Hrs	Fitted Curve, % Removal	Raw Data, % Removal	
0	0		
0.5	82.74933706	82.821	
1	85.780731663	84.781	
2	85.895850302	91.642	
3	85.896004792	93.602	
5	85.896005	80.371	
7	85.896005	94.583	
10	85.896005	91.642	
12	85.896005	89.682	
14	85.896005	88.702	
16	85.896005	86.251	
18	85.896005	86.742	
20	85.896005	85.761	
22	85.896005	80.371	
24	85.896005	80.371	
26	85.896005	81.841	
28	85.896005	79.881	
30	85.896005	77.92	

CONTROL PANEL Soil Type : LAAP Site 2 Extractant : .05 M EDTA Contaminant : Cd Curve Type : 1st Order			Lo : 62.1 k : 1.4
Time, Hrs	Fitted Curve, % Removal	Raw Data, % Removal	
0	0		
0.5	49.340129791	40.916	
1	59.474126003	81.833	
2	61.983058453	40.916	
3	62.088898462	49.099	
5	62.093551704	57.283	
7	62.093559985	57.283	
10	62.09356	57.283	
12	62.09356	57.283	
14	62.09356	57.283	
16	62.09356	49.099	
18	62.09356	65.466	
20	62.09356	65.466	
22	62.09356	73.649	
24	62.09356	65.466	
26	62.09356	65.466	
28	62.09356	98.199	
30	62.09356	57.283	

CONTROL PANEL Soil Type : LAAP Site 2 Extractant : .05 M EDTA Contaminant : Cr Curve Type : 1st Order			Lo : 53.5 k : 328.0
Time, Hrs	Fitted Curve, % Removal	Raw Data, % Removal	
0	0		
0.5	53.493012	11.501	
1	53.493012	96.071	
2	53.493012	3.382	
3	53.493012	0	
5	53.493012	0	
7	53.493012	0	
10	53.493012	0	
12	53.493012	0	
14	53.493012	0	
16	53.493012	0	
18	53.493012	0	
20	53.493012	0	
22	53.493012	0	
24	53.493012	0	
26	53.493012	0	
28	53.493012	0	
30	53.493012	0	

CONTROL PANEL Soil Type : LAAP Site 2 Extractant : .05 M DTPA Contaminant : Cd Curve Type : 1st Order			Lo : 92.4 k : 0.9
Time, Hrs	Fitted Curve, % Removal	Raw Data, % Removal	
0	0		
0.5	60.426009624	66.309	
1	81.328899402	74.819	
2	91.061070268	83.152	
3	92.225664287	89.889	
5	92.381701161	91.13	
7	92.38393554	91.662	
10	92.383967944	95.031	
12	92.383967999	93.79	
14	92.383968	95.031	
16	92.383968	87.23	
18	92.383968	97.69	
20	92.383968	97.86	
22	92.383968	97.33	
24	92.383968	93.79	
26	92.383968	99.995	
28	92.383968	99.995	
30	92.383968	72.16	

CONTROL PANEL Soil Type : LAAP Site 2 Extractant : .05 M DTPA Contaminant : Cr Curve Type : 1st Order			Lo : 10.0 k : 124.5
Time, Hrs	Fitted Curve, % Removal	Raw Data, % Removal	
0	0		
0.5	10.019204	37.6	
1	10.019204	100	
2	10.019204	6	
3	10.019204	7.2	
5	10.019204	4.8	
7	10.019204	4.4	
10	10.019204	4	
12	10.019204	4	
14	10.019204	4.8	
16	10.019204	4	
18	10.019204	4.4	
20	10.019204	4.4	
22	10.019204	4	
24	10.019204	4	
26	10.019204	9.2	
28	10.019204	4	
30	10.019204	4.4	

CONTROL PANEL Soil Type : LAAP Site 2 Extractant : .05 M Citric Contaminant : Cd Curve Type : 1st Order			Lo : 96.0 k : 0.4
Time, Hrs	Fitted Curve, % Removal	Raw Data, % Removal	
0	0		
0.5	35.42809493	73	
1	57.781711627	79.637	
2	80.785025352	86.273	
3	89.942809493	89.591	
5	95.04	92.91	
7	95.847850254	96.228	
10	95.9904	96.228	
12	95.998478503	96.228	
14	95.999758859	96.228	
16	95.999961782	96.228	
18	95.999993943	96.228	
20	95.99999904	99.546	
22	95.999999848	96.228	
24	95.999999976	96.228	
26	95.999999996	96.228	
28	95.999999999	96.228	
30	96	96.228	

CONTROL PANEL		
Soil Type	: LAAP Site 2	Lo : 90.0
Extractant	: .05 M Citric	k : 0.2
Contaminant : Cr		
Curve Type : 1st Order		

Time, Hrs	Fitted Curve, % Removal	Raw Data, % Removal
0	0	
0.5	18.510458875	41.178
1	33.213838997	52.888
2	54.17035465	64.012
3	67.393022116	72.794
5	81	77.673
7	86.417035465	80.991
10	89.1	84.113
12	89.641703547	86.455
14	89.857359613	88.602
16	89.943213839	90.554
18	89.977393022	93.286
20	89.991	93.481
22	89.996417035	96.799
24	89.998573596	95.433
26	89.999432138	97.189
28	89.99977393	98.75
30	89.99991	98.36

Soil Type : LAAP Site 2
Extractant : .05 M Citric
Contaminant : Cr
Curve Type : 1st Order

Lo : 90.0
k : 0.2

Time, Hrs	Fitted Curve, % Removal	Raw Data, % Removal
0	0	
0.5	18.510458875	41.178
1	33.213838997	52.888
2	54.17035465	64.012
3	67.393022116	72.794
5	81	77.673
7	86.417035465	80.991
10	89.1	84.113
12	89.641703547	86.455
14	89.857359613	88.602
16	89.943213839	90.554
18	89.977393022	93.286
20	89.991	93.481
22	89.996417035	96.799
24	89.998573596	95.433
26	89.999432138	97.189
28	89.99977393	98.75
30	89.99991	98.36

CONTROL PANEL		
Soil Type	: Polk #5-8	Lo : 89.5
Extractant	: .05 M HNO ₃	k : 0.1
Contaminant : Pb		
Curve Type : 1st Order		
Time, Hrs	Fitted Curve, % Removal	Raw Data, % Removal
0	0	
0.5	9.2725413575	27.982
1	17.584412064	34.093
2	31.713946501	42.727
3	43.067396516	50.196
5	59.520593195	60.127
7	70.143669213	66.905
10	79.457934834	70.596
12	83.016298157	78.953
14	85.313770485	81.516
16	86.79714321	85.925
18	87.754889083	87.771
20	88.373261756	89.514
22	88.772516688	89.463
24	89.030297323	88.745
26	89.19673448	89.002
28	89.304195335	93.103
30	89.37357789	85.977

Soil Type : Polk #5-8
Extractant : .05 M HNO₃
Contaminant : Pb
Curve Type : 1st Order

Lo : **89.5**
k : **0.1**

Time, Hrs	Fitted Curve, % Removal	Raw Data, % Removal
0	0	
0.5	9.2725413575	27.982
1	17.584412064	34.093
2	31.713946501	42.727
3	43.067396516	50.196
5	59.520593195	60.127
7	70.143669213	66.905
10	79.457934834	70.596
12	83.016298157	78.953
14	85.313770485	81.516
16	86.79714321	85.925
18	87.754889083	87.771
20	88.373261756	89.514
22	88.772516688	89.463
24	89.030297323	88.745
26	89.19673448	89.002
28	89.304195335	93.103
30	89.37357789	85.977

CONTROL PANEL		
Soil Type : Polk #5-8	Lo :	65.0
Extractant : .05 M EDTA	k :	0.1
Contaminant : Pb		
Curve Type : 1st Order		
Time, Hrs	Fitted Curve, % Removal	Raw Data, % Removal
0	0	
0.5	7.0686890213	28.586
1	13.368664743	32.456
2	23.987772609	35.407
3	32.422829814	41.527
5	44.445195209	43.806
7	52.030794953	49.138
10	58.5	50.744
12	60.898777261	49.766
14	62.412303391	55.316
16	63.36727382	57.011
18	63.969819425	59.479
20	64.35	61.101
22	64.589877726	66.14
24	64.741230339	65.629
26	64.836727382	68.185
28	64.896981942	69.047
30	64.935	71.691

CONTROL PANEL		
Soil Type : Polk #5-8	Lo :	42.2
Extractant : .05 M Citric	k :	0.3
Contaminant : Pb		
Curve Type : 1st Order		
Time, Hrs	Fitted Curve, % Removal	Raw Data, % Removal
0	0	
0.5	13.047429718	61.857
1	22.056931824	60.706
2	32.574049926	60.023
3	37.588789693	56.162
5	41.120025403	57.229
7	41.922867262	57.357
10	42.133497099	58.743
12	42.153284477	59.874
14	42.157783224	59.319
16	42.158806034	59.532
18	42.159038574	61.623
20	42.159091443	60.919
22	42.159103463	61.665
24	42.159106196	60.812
26	42.159106817	62.519
28	42.159106958	63.287
30	42.159106991	64.609

CONTROL PANEL		
Soil Type : Polk #5-8	Lo :	94.7
Extractant : .05 M DTPA	k :	0.03
Contaminant : Pb		
Curve Type : 1st Order		
Time, Hrs	Fitted Curve, % Removal	Raw Data, % Removal
0	0	
0.5	3.4430845834	14.676
1	6.7610163636	18.277
2	13.039452891	23.848
3	18.869754595	28.139
5	29.311616196	34.32
7	38.316061714	39.831
10	49.552868131	47.139
12	55.770923425	50.608
14	61.13300753	53.546
16	65.756952572	60.675
18	69.744370027	67.586
20	73.182883637	74.304
22	76.148054949	74.072
24	78.705043784	79.981
26	80.910040128	82.236
28	82.81149891	83.297
30	84.451204803	90.924

CONTROL PANEL		
Soil Type : WES	Lo :	50.0
Extractant : .05 M HNO ₃	k :	0.4
Contaminant : Pb		
Curve Type : 1st Order		
Time, Hrs	Fitted Curve, % Removal	Raw Data, % Removal
0	0	
0.5	21.228003133	57.7
1	30.094641472	41.9
2	42.075534038	30.9
3	46.845213278	24.2
5	49.5	19.2
7	49.92075534	14.9
10	49.995	10.4
12	49.999207553	7.9
14	49.999874406	5.9
16	49.999980095	4.4
18	49.999996845	3.9
20	49.9999995	3.3
22	49.999999921	2.7
24	49.999999987	3.1
26	49.999999998	3.1
28	50	1.7
30	50	1.5

CONTROL PANEL Soil Type : WES Extractant : .05 M HNO₃ Contaminant : Cd Curve Type : 1st Order			Lo : 85.0 k : 5.0
Time, Hrs	Fitted Curve, % Removal	Raw Data, % Removal	
0	0		
0.5	84.915	89.7	
1	84.99915	87	
2	84.999999992	84.5	
3	85	87.5	
5	85	85.9	
7	85	87.1	
10	85	86.1	
12	85	84.9	
14	85	82.9	
16	85	75	
18	85	84.1	
20	85	80.9	
22	85	76.8	
24	85	77.1	
26	85	1	
28	85	67	
30	85	72	

CONTROL PANEL Soil Type : WES Extractant : .05 M HNO₃ Contaminant : Cr Curve Type : 1st Order			Lo : 10.0 k : 0.0
Time, Hrs	Fitted Curve, % Removal	Raw Data, % Removal	
0	0		
0.5	0.2918649674		
0.6	0.4345872959	17.3	
1	0.7137681826	0.7	
2	1.3765895634	0.7	
3	1.9921014415	0.6	
5	3.0944606398	0.4	
7	4.0450701883	0.4	
10	5.2313526145	0.4	
12	5.8877997798	0.4	
14	6.4538810938	0.3	
16	6.9420362278	0.4	
18	7.362992421	0.4	
20	7.7260002113	0.4	
26	8.5417649053	0.5	
28	8.7425040703	0.4	
30	8.9156096853	0.4	

REPORT DOCUMENTATION PAGE

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13. ABSTRACT (Maximum 200 words) <p>The purpose of the research was to design a pilot-scale soil washing system and to determine its optimal operating conditions to effectively remediate soils contaminated with heavy metals. The research focused on eight contaminated soils from Army installations and the metal extraction capabilities of eight extracting agents including HNO₃, HCl, fluorosilicic acid, citric acid, EDTA, DTPA, NTA, and NaOH. These extracting agents were tested at concentrations of 0.01 M, 0.05 M, and 0.1 M.</p> <p>Among the solid-to-liquid ratios of 0.005, 0.01, 0.05, 0.2, and 0.5, the most efficient and effective ratio for the removal of heavy metals was a solid-to-liquid ratio of 0.05. In evaluating the extracting agents for removal of heavy metals from soil, citric acid, HCl, HNO₃, and DTPA were the most effective reagents for the removal of lead (Pb). HNO₃, HCl, EDTA, and citric acid were the most effective for the removal of cadmium (Cd). Citric acid was most effective for the removal of chromium (Cr). The reaction times to reach chemical equilibrium between the metal-contaminated soils and extracting agents varied from 30 min to 30 hr depending on the soil type, the heavy metal contaminant, and the type and concentration of extracting agent.</p>																
14. SUBJECT TERMS <table border="0"> <tr> <td>Acid extraction</td> <td>Extraction</td> <td>Lead</td> <td>Soil washing</td> </tr> <tr> <td>Cadmium</td> <td>Heavy metals</td> <td>Remediation</td> <td></td> </tr> <tr> <td>Chromium</td> <td>Installation Restoration Research Program</td> <td>Soil contamination</td> <td></td> </tr> </table>			Acid extraction	Extraction	Lead	Soil washing	Cadmium	Heavy metals	Remediation		Chromium	Installation Restoration Research Program	Soil contamination		15. NUMBER OF PAGES 135 16. PRICE CODE	
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